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Modeling of Decay Rate for Molecules at an Island Surface

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THESIS APPROVAL

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ABSTRACT

An abstract of the thesis of Ting Xiong for the Master of Science in Physics presented June 7, 1995

Title: Modeling of Decay Rate for Molecules at an Island Surface

The decay rates for molecules at rough surfaces are studied via an island surface model, with particular emphasis on the effect due to the *distribution* of surface roughness. Two extreme cases are studied when the surface islands distribute themselves evenly and when they coalesce to form local clusters at the molecule-substrate interface. The optical properties of the interfacial layer in these two cases are described by the Maxwell-Garnett and the fractal-cluster models, respectively. Among other results, it is found that both enhancement and suppression of the surface-induced decay rates are possible due to the presence of roughness, with more dramatic suppression taking place when the surface islands coalesce to form clusters.

MODELING OF DECAY RATE FOR MOLECULES AT AN ISLAND SURFACE

by

TING XIONG

A thesis submitted in partial fulfillment of the
requirements for the degree of

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TO MY FAMILY

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CHAPTER I

INTRODUCTION

The behavior of an excited fluorescing molecule near an interface of two different media has been studied both theoretically and experimentally in the last two decades. One of the problems is to explain the variation of lifetimes of the fluorescing molecule as a function of the distance from the interface. One theoretical approach was put forth by Chance, Prock and Silbey (CPS) [1] in 1975. In their theory, CPS made an analogy with Sömmerfeld's [2] 1909 treatment of a radiating antenna near the earth. The antenna was treated as an oscillating dipole with its size much smaller compared to the dipole-surface distance. To a great extent, the electrodynamics for a system of a fluorescing molecule above a substrate is very similar to that of a radiating antenna above the earth. The results from CPS theory were quite successful in explaining the experimental data from the work done by Drexhage and collaborators [3], in which the fluorescent lifetimes of an electronically excited molecule were measured near metallic surfaces, using the fatty-acid monolayer assembly technique developed by Kuhn and co-workers [4].

However, in the 1980's, the limitation of the CPS theory was observed when comparison was made with the experimental data obtained by Harris et al and others [5] at close molecule surface distances ($d<100$Å). Experimentally, one assumption of the CPS theory that the interface is perfectly flat can only be valid when the molecule-surface distance is large compared to the morphological protrusion from the surface. When the molecule is moved close to the surface, the interfacial roughness, together with other possible effects such as surface damping [5, 6] and non-local dielectric response of the substrate [7, 8] would be very significant, leading to the failure of CPS theory. While all

these effects or different combinations among them are plausible for explaining the data observed in a particular " close-distance experiment ", we shall address specifically the effects due to surface roughness in this present work.

Previous works have already studied this problem by modeling the surface as both a randomly (Gaussian-distributed) [9] or periodically roughened substrate [10]. Among other results, it was pointed out that the presence of roughness could lead to a suppression of nonradiative decay and hence an *enhancement* of fluorescence compared to the flat surface case, due to a re-coupling of the non-radiative surface plasmon to radiative modes [10]. Recent experiment performed by Ahmadi and Rusling [11] has indeed revealed the possibility of observing enhanced fluorescence from pyrene adsorbed at a rough silver electrode.

Aside from "extended" surface morphologies, "localized" structures have also been considered in the literature with most of the works adopting the "island surface model". In particular, the cases of an isolated surface island [11, 12] as well as a two-dimensional array of islands [13] have all been studied previously. While the single island case has been studied very thoroughly taking into consideration also of the non-local dielectric response of the substrate [8], the case for a "two-island" or "many-island" substrate usually becomes quite mathematically complicated. Previous treatment has been limited to a static theory with local dielectric response from the substrate and the islands are modeled as a 2D square periodic array of interacting spheres [13]. Detailed numerical results of up to a "five-sphere" substrate were worked out and it was found that the nonradiative decay rates are quite insensitive to the geometry of the clustering spheres as long as the molecule is not located in the "cavity-site" (i.e. the space between two islands).

An alternative and simpler approach would be to apply mean-field theory to calculate an "effective" dielectric response for the two-dimensional island layer at the

interface. To this end, the theories of Maxwell-Garnett [14, 15] and Bruggemen [16] have often been applied. Moreover, these previous investigations have all assumed that the distribution of the surface islands is uniform throughout the interface layer [15, 16] which may not be very realistic for certain kinds of interfaces. In fact, recent experiment on the fluorescence of R6G and malachite on porous silica surfaces has revealed fractal nature for the substrate surface [18]. More recently, scanning tunneling microscopy studies of metal-on-metal growth at submonolayer coverages have also revealed formation of fractal-like islands at the interface [19]. Hence, it is of interest to go beyond the "uniform-distribution" assumption for the islands to model the interfacial roughness.

It is the purpose of this thesis to study the effect of "distribution of roughness" at the interface on the decay rates of the admolecules. We shall look at the extreme case when the surface islands coalesce to form clusters and compare with the results in the other extreme when they disperse themselves uniformly throughout the interfacial layer. Previously, a model based on 3D fractal-clustering has been applied to study the effect due to particle-clustering in a composite material on fluorescing lifetimes of admolecule [20]. However, in our present case of a slightly roughened interface, two-dimensional clusters tend to form more likely due to the low concentration of the islands. Using effective medium theory we can calculate the dielectric function of such a single 2D cluster, and then the whole layer on which the clusters are randomly dispersed. Once we obtain an effective dielectric function for the interfacial island layer, we can then apply the CPS theory (for a stratified multi-layer geometry) to study the roughness effect on the molecular lifetimes subject to different distributions of the interfacial islands.

CHAPTER II

THEORETICAL MODELING OF A FLUORESCING MOLECULE INTERACTING WITH A SUBSTRATE SURFACE

In this chapter we will briefly review a phenomenological approach to the theoretical modeling of a fluorescing molecule at an interface. The approach models the fluorescing molecule as a radiating dipole, and surface-induced effects are accounted for by solving the "Sömmerfeld-type" problem which depends crucially on the boundary geometry as well as the dielectric (optical) properties of the substrate.

MODELING OF THE SURFACE-MODIFIED DYNAMICS OF A FLUORESCING MOLECULE

When a fluorescing molecule is placed near a substrate surface, the lifetime of the molecule will be affected by the electromagnetic field reflected from the interface. The approach to the modeling of the fluorescing molecule is to consider it as a radiating dipole oscillating at the molecule position, and calculate the reflected field at the dipole position and the effects of this field. The geometry of the problem is shown in *Fig. 1.*

For an oscillating dipole in the vicinity of a metal surface and with the intrinsic damping effects accounted for, the equation of motion can be obtained as follows:

$$\sum \vec{F} = \vec{F}_{external} + \vec{F}_{system} + \vec{F}_{damping} ,$$

$$\Rightarrow \qquad \sum \vec{F} = -e\vec{E}_r - m\gamma_0 \dot{\vec{r}} - m\omega^2 \vec{r} = m\ddot{\vec{r}} \ , \tag{2.1}$$

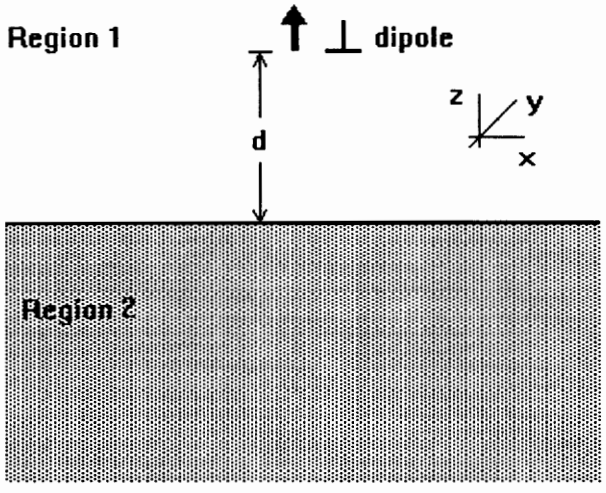

Fig.1 The.geometry of the "single mirror" case. The distance from the dipole to the interface is d. The two semi-infinite regions are with dielectric functions $\varepsilon_1 = n_1^2$ *and* $\varepsilon_2 = n_2^2 - k_2^2 + 2in_2k_2$, *where* n_j *and* k_j *are the optical constants of the media.*

and hence

$$m\ddot{\vec{r}} + m\omega^2 \vec{r} + m\gamma_0 \dot{\vec{r}} = -e\vec{E}_r \ , \tag{2.2}$$

Following Chance, Prock, Silbey (CPS) [1], and the references therein, Eqn. (2.2) can be expressed in terms of the dipole moment, $\vec{\mu}$, by multiplying both sides of (2.2) by $-e$. This will give us

$$\ddot{\vec{\mu}} + \gamma_0 \dot{\vec{\mu}} + \omega_0^2 \vec{\mu} = \frac{e^2}{m} \vec{E}_r, \tag{2.3}$$

where ω_0 and γ_0 refer to the intrinsic transition frequency and level width (decay rate) for an isolated (free) molecule, and the dipole is driven by the field ($\vec{E}_r$) reflected from the boundary of the substrate, this then provides a mechanism to account for the modifications of the molecular properties due to the presence of the surface as we show below. Assuming $\vec{\mu}$ and $\vec{E}$ oscillate at the same complex frequency, the solution is expected to have the following form:

$$\vec{\mu} = \vec{\mu}_0 \left\{ e^{-i(\omega+\Delta\omega)t} e^{-\gamma t/2} \right\}, \tag{2.4}$$

$$\vec{E}_r = \vec{E}_0 \left\{ e^{-i(\omega+\Delta\omega)t} e^{-\gamma t/2} \right\}, \tag{2.5}$$

the expression $\Delta\omega$ is the frequency shift caused by the reflected E-field. The physical solutions are obtained from the real part of the above expressions. Let us write (2.4) and (2.5) as :

$$\vec{\mu} = \vec{\mu}_0 e^{-\gamma' t}, \tag{2.6}$$

$$\vec{E}_r = \vec{E}_0 e^{-\gamma' t}, \tag{2.7}$$

where

$$\gamma' = i(\omega + \Delta\omega) + \gamma/2. \tag{2.8}$$

Substituting this into equation (2.3) yield

$$\vec{\mu}_0(\gamma'^2-\gamma_0\gamma'+\omega^2)e^{-\gamma' t}=\frac{e^2}{m}\vec{E}_0 e^{-\gamma' t}. \tag{2.9}$$

From this we can solve the quadratic equation

$$\gamma'^2-\gamma_0\gamma'+\omega^2-\frac{e^2E_0}{m\mu_0}=0\ , \tag{2.10}$$

to obtain

$$\gamma'=\frac{\gamma_0}{2}\pm\left[\frac{\gamma_0{}^2}{4}-\omega^2+\frac{e^2E_0}{m\mu_0}\right]^{\frac{1}{2}}\ , \tag{2.11}$$

pulling $-\omega^2$ out of the radical and binomially expanding:

$$\gamma'=\frac{\gamma_0}{2}\pm i\omega\left[1-\frac{\gamma_0{}^2}{4\omega^2}-\frac{e^2E_0}{m\omega^2\mu_0}\right]^{\frac{1}{2}} \tag{2.12}$$

$$\gamma'\cong\frac{\gamma_0}{2}\pm i\omega\left[1-\frac{1}{2}\left(\frac{\gamma_0{}^2}{4\omega^2}+\frac{e^2E_0}{m\omega^2\mu_0}\right)\right] \tag{2.13}$$

where the last term in (2.13) is $\frac{1}{\mu_0}$ times the induced dipole moment, $\frac{e^2}{m\omega^2}\left|\vec{E}_0\right|$.

From (2.6) to (2.8) we obtain

$$\vec{\mu}=\vec{\mu}_0 e^{-i(\omega+\Delta\omega)t}e^{-\gamma t/2}, \tag{2.14}$$

$$\vec{E} = \vec{E}_0 e^{-i(\omega+\Delta\omega)t} e^{-\gamma t/2}. \tag{2.15}$$

From (2.13), we have

$$\gamma' = \frac{\gamma_0}{2} \pm i\omega\left[1 - \left(\frac{\gamma_0^{\,2}}{8\omega^2} + \frac{e^2 E_0}{2\omega^2 m\mu_0}\right)\right], \tag{2.16}$$

and since from (2.8),

$$\gamma' = i(\omega + \Delta\omega) + \frac{\gamma}{2}, \tag{2.17}$$

hence from (2.16) and (2.17), we obtain

$$\gamma' = \frac{\gamma_0}{2} \pm i\omega\left[1 - \left(\frac{\gamma_0^{\,2}}{8\omega^2} + \frac{e^2 E_0}{2\omega^2 m\mu_0}\right)\right] = i(\omega + \Delta\omega) + \frac{\gamma}{2}. \tag{2.18}$$

In (2.18) the $\pm$ is the result of the two roots of the quadratic equation. Since physically we expect that $\gamma > \gamma_0$ for most cases, we chose '+' sign in equation (2.18):

$$\frac{\gamma_0}{2} + i\omega\left[1 - \left(\frac{\gamma_0^{\,2}}{8\omega^2} + \frac{e^2 E_0}{2\omega^2 m\mu_0}\right)\right] = i(\omega + \Delta\omega) + \frac{\gamma}{2}. \tag{2.19}$$

Comparing real and imaginary parts on both side and noting that E_0 is complex in general, we finally obtain:

$$\hat{\gamma} = \frac{\gamma}{\gamma_0} = 1 + \frac{3qn_1^{\,2}}{2\mu_0 k_1^{\,3}} \mathrm{Im}(E_0), \tag{2.20}$$

where q is the intrinstic quantum yeild and $\gamma_0 = \frac{2}{3}\frac{e^2k_1^3}{m\omega n_1^2 q}$ [1].

Hence, all the surface effects on the fluorescing properties of the molecule can be accounted for by calculating the field (E_0) refelected from the interface acting on the dipole.

CALCULATION OF REFLECTED FIELD

The problem is now reduced to the calculation of the reflected electric field at the dipole position. In this section we consider only one single interface.

Fig. 1 shows the geometry of the case of a single mirror. The two regions are semi-infinite space with dielectric functions $\varepsilon_1 = n_1^2$ and $\varepsilon_2 = n_2^2 - k_2^2 + 2in_2k_2$. The electric field at any point of *Region 1* can be written as

$$\vec{E} = \frac{1}{\varepsilon}\left[k^2\vec{\Pi}_1 + \vec{\nabla}\left(\vec{\nabla}\cdot\vec{\Pi}_1\right)\right], \tag{2.21}$$

where k is the wave number, and Π_1 is the Hertz vector of *Region 1* which we now construct. Following CPS [1], we first consider the dipole oriented perpendicular to the interface. In cylindrical coordinates (r, z, ϕ) and following Sömmerfeld [2], we can write the Hertz vectors in the two media as follows:

$$\Pi_1 = \hat{e}_z \mu k_1 \int_0^\infty du J_0(ur)\frac{u}{l_1}\left(e^{\pm l_1(\hat{z}-\hat{d})} + f_1 e^{-l_1\hat{z}}\right), \tag{2.22}$$

$$\Pi_2 = \hat{e}_z \mu k_1 \int_0^\infty f_2 e^{l_2\hat{z}} J_0(ur)\frac{u}{l_2}du, \tag{2.23}$$

where $\hat{d} \equiv k_1 d$, $l_j = -i\left(\frac{\varepsilon_j}{\varepsilon_1} - u^2\right)^{\frac{1}{2}}$ and, since the geometry is cylindrical symmetric, the solution to the differential equation should be related to $J_0(ur)$, the zeroth-order Bessel function. The first term in (2.22) is the source field for $z < d$ which is the region of interest here for the reflected field calculation. Apply the boundary conditions at $z = 0$ and solving for f_1 and f_2,

$$\varepsilon_1 \Pi_1 = \varepsilon_2 \Pi_2, \tag{2.24}$$

and

$$\frac{\partial \Pi_1}{\partial z} = \frac{\partial \Pi_2}{\partial z}, \tag{2.25}$$

we obtain:

$$f_1 = -R^{\parallel} e^{-l_1 \hat{d}}, \tag{2.26}$$

$$f_2 = \frac{\varepsilon_1}{\varepsilon_2}\left(1 - R^{\parallel}\right) e^{-l_1 \hat{d}}, \tag{2.27}$$

where the $R^{\parallel}$ is the reflection coefficient for an incident ray polarized parallel to the plane of incidence (p-polarized)

$$R^{\parallel} = \frac{\varepsilon_1 l_2 - \varepsilon_2 l_1}{\varepsilon_1 l_2 + \varepsilon_2 l_1}. \tag{2.28}$$

For the perfect mirror ($R^{\parallel} = -1$), f_1 becomes $e^{-l_1 \hat{d}}$. Ignoring the source term, we finally obtain the reflected field at the dipole position as [1]

$$E_R^{\parallel} = -\frac{k_1^3}{\varepsilon_1}\mu_0 \int_0^{\infty} R^{\parallel} e^{-2l_1\hat{d}} \frac{u^3}{l_1} du \tag{2.29}$$

and we can finally get from Eqn. (2.20):

$$\hat{\gamma} = \frac{\gamma}{\gamma_0} = 1 - \frac{3}{2} q \,\mathrm{Im}\left(\int_0^{\infty} R^{\parallel} e^{-2l_1\hat{d}} \frac{u^3}{l_1} du \right). \tag{2.30}$$

CASE OF A ROUGH INTERFACE

Our main interest in this thesis is to extend the above formulation to the case of a rough metallic interface. The induced molecular decay rate (γ) at such a surface has been studied previously by many people modeling the surface morphology either with Gaussian-distributed (random)[9] or periodic roughness [10]. However, most of these had followed a perturbative approach which limits the modeling to the case of very shallow roughness. In the present study, we would like to model surface roughness as a collection of spherical islands of unlimited sizes and apply a mean-field treatment to calculate the optical response of this "island-surface layer". The decay rate at an island surface has also been studied before, except that the distribution in these "islands" at the interface was restricted to be uniform in the previous case [15, 16]. Here we would like to study the effect of the other extreme case when the islands coalesce to form local clusters. The results of the decay rates obtained in this case will be compared with those obtained previously assuming uniform distribution of islands [15, 16]. In this latter case, we follow previous work [15] and apply the Maxwell-Garnett theory to calculate the dielectric function of *Region 2*, the island surface layer. We have also developed a two-dmension fractal cluster (2-D FC) model to simulate the effect due to the islands when coalescence among them occurs.

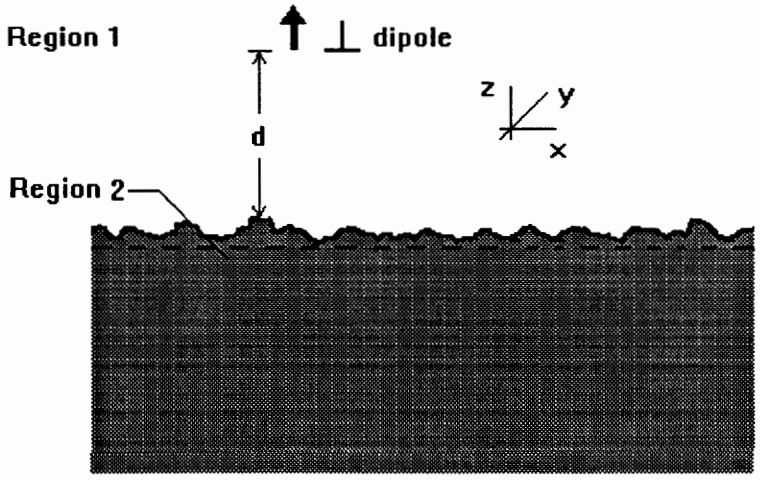

Fig. 2 The geometry of the problem of a perpendicular dipole near a rough interface.

Let us explain briefly the effective-medium modeling of the roughened interfacial layer as follows. *Fig 2* presents a schematic drawing of the problem shown with the actual roughened morphology of the interface. We shall model these surface "bumps" as a collection of islands as shown in *Fig. 3*. To further simplify the modeling, we assume these islands are spherical and of identical size.

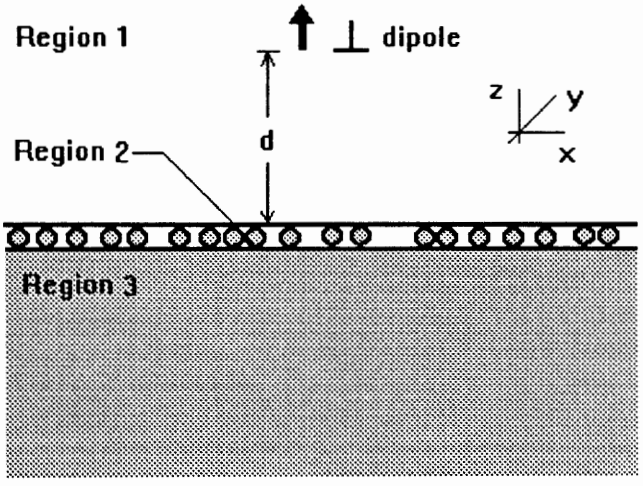

Fig.3 The "island surface": Particles (islands) are dispersed thoughout the surface.

According to the mean field approach, the dielectric response of this heterogeneous interfacial island layer (Region 2) will be described by certain effective response function averaging over the dielectric properties of each of the constituents and the "host", i.e., *medium 1* and the spheres of material same as that for *medium 2*.

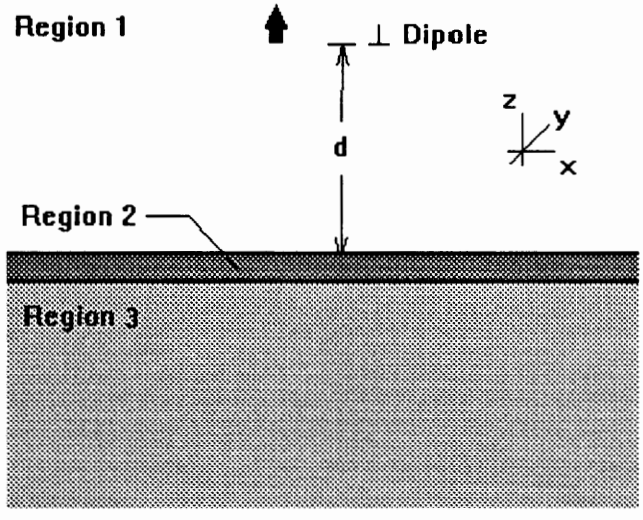

Fig. 4 Effective medium treatment of the dielectric response of the roughened interfacial layer.

Hence, the roughened interfacial layer is finally replaced by a homogeneous thin film layer with this effective dielective function as shown in *Fig 4*.

FLUORESCING MOLECULE AT A THIN FILM INTERFACIAL LAYER

According to the above description, we will ultimately have to solve the problem of a dipole near a thin film at the top a thick substrate. This problem has also been studied

by CPS and we briefly summarize their results for this case in the following. It turns out that for a stratified layered system with mutiple (flat) interfaces, the general solution can be obtained by application of the Green function technique.

In the case of a metal film of thickness d_2, the dyadic Green function can be computed by satisfying the boundary conditions at both interfaces.

The boundary conditions on $\mathbf{E}$ and $\mathbf{H}$ at an interface can be written as the continuity of both $\hat{e}_z \times \mathrm{G}$ and $\hat{e}_z \times \nabla \times \mathrm{G}$ across the interface. So at $z = 0$ (interface between Region 1 and Region 2) and $z = -d_2$ (interface between Region 2 and Region 3), we have,

$$\left.\begin{aligned} \hat{e}_z \times \left(\mathrm{G}_0 + \mathrm{G}_S^{(\mathrm{I})}\right) &= \hat{e}_z \times \mathrm{G}_S^{(\mathrm{II})} \\ \hat{e}_z \times \nabla \times \left(\mathrm{G}_0 + \mathrm{G}_S^{(\mathrm{I})}\right) &= \hat{e}_z \times \nabla \times \mathrm{G}_S^{(\mathrm{II})} \end{aligned}\right\} \quad z = 0, \tag{2.31}$$

and

$$\left.\begin{aligned} \hat{e}_z \times \left(\mathrm{G}_0 + \mathrm{G}_S^{(\mathrm{II})}\right) &= \hat{e}_z \times \mathrm{G}_S^{(\mathrm{III})} \\ \hat{e}_z \times \nabla \times \left(\mathrm{G}_0 + \mathrm{G}_S^{(\mathrm{II})}\right) &= \hat{e}_z \times \nabla \times \mathrm{G}_S^{(\mathrm{III})} \end{aligned}\right\} \quad z = -d_2. \tag{2.32}$$

Since the reflected field can be in terms of the Green function in the form [1]

$$\vec{\mathbf{E}}_R = i\omega \int \mathrm{G}_s\left(\mathbf{R}|\mathbf{R}'\right) \cdot \mathrm{J}(\mathbf{R}') d\mathbf{R}'. \tag{2.33}$$

by solving (2.31) and (2.32), we finally obtain for a perpendicular dipole located at $z = d$:

$$\vec{\mathbf{E}}_R = \vec{\mathbf{E}}_z(d)\hat{z} = \hat{z}\frac{i\mu_0}{n_1^2}\int_0^\infty \frac{\lambda^3}{h_1} f_1' e^{2ih_1 d} d\lambda \tag{2.34}$$

where $h_i^2 = k_i^2 - \lambda^2$,

$$f'_1 = \frac{S_1 h_1 \varepsilon_2 - h_2 \varepsilon_1}{S_1 h_1 \varepsilon_2 + h_2 \varepsilon_1},$$

$$S_1 = \frac{h_2 \varepsilon_3 - i h_3 \varepsilon_2 \tan\varphi}{h_3 \varepsilon_2 - i h_2 \varepsilon_3 \tan\varphi}, \tag{2.35}$$

with $\varphi = h_2 d_2$. Note that as $d_2 \to 0$, both R_1 and $S_1 \to 0$, giving back the results for the case of a single interface. The calculation of the emission rate of the perpendicular case was given by CPS, the final results can be expressed as

$$\hat{\gamma} = 1 - \frac{3}{2} q \int_0^\infty \left(\frac{R_{12}^{\perp} + R_{23}^{\parallel} e^{-2 l_2 \hat{d}_2}}{1 + R_{12}^{\perp} R_{23}^{\parallel} e^{-2 l_2 \hat{d}_2}} \right) e^{-2 l_1 \hat{d}_1} \frac{u^3 du}{l_1} \tag{2.36}$$

where $R_{ij}^{\perp} = \dfrac{\varepsilon_i l_j - \varepsilon_j l_i}{\varepsilon_i l_j + \varepsilon_j l_i}$ are the Fresnel coefficients at interface *(i, j)*, and

$$\begin{aligned} l_1 &= -i\left(1 - u^2\right)^{\frac{1}{2}} \\ l_2 &= -i\left(\varepsilon_2/\varepsilon_1 - u^2\right)^{\frac{1}{2}}. \end{aligned} \tag{2.37}$$

CHAPTER III

FRACTAL-CLUSTER MODELING OF THE ROUGHENED INTERFACIAL LAYER

In this chapter we will discuss the theoretical models applied to simulate the island surface in the calculation of the interaction of the fluorescing molecule and the rough interface. We will first review briefly the model of Maxwell-Garnett [14] in the case where the particles dispersed randomly and uniformly throughout the layer. We shall then formulate the fractal-cluster model which applies to the case where the particles coalesce to form local clusters.

MAXWELL-GARNETT THEORY

To model the case when the surface islands are dispersed uniformly throughout the layer, we follow the previous work [15] to adopt the Maxwell-Garnett (MG) model to determine the average dielectric function (ε) of the interfacial layer. The MG model is an effective medium theory which is accurate for small particle concentration. Let us assume a host (dielectric function ε_m) with k particles (dielectric function ε) dispersing randomly throughout the medium. (See *Fig. 5*)

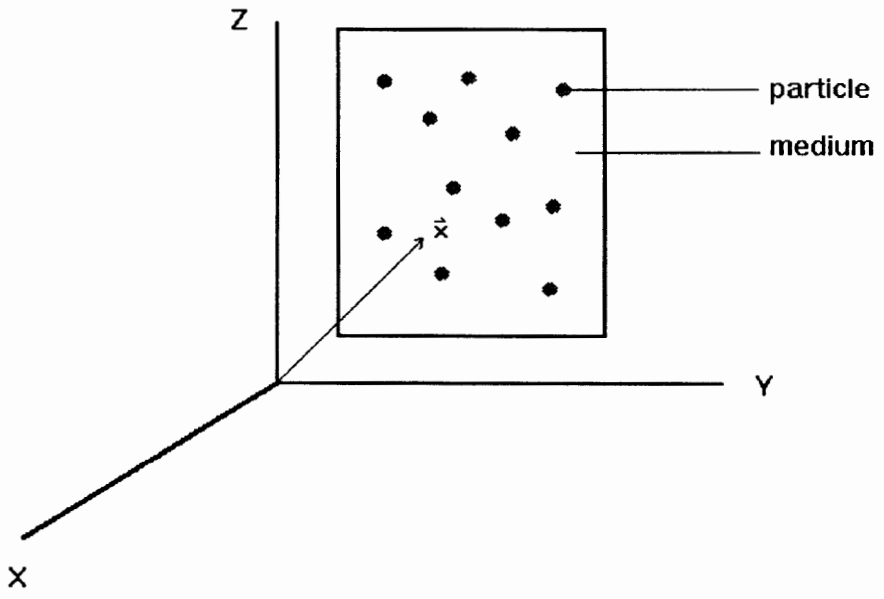

Fig. 5 Dispersion of particles in a host medium

Following the approach of Bohren and Huffman[21], here we consider a model for an inhomogeneous medium of a two-component mixture composed of inclusions embedded in an otherwise homogeneous host, where ε and ε_m. are their respective dielectric functions. The inclusions are identical in composition but may be different in volume, shape and orientation. Here we limit ourselves to ellipsoidal inclusions. The average of $\vec{E}$ field at the position x can written as [21]

$$\left\langle \vec{E}(\vec{x}) \right\rangle = \frac{1}{V}\int_V \vec{E}\left(\vec{x}+\vec{\xi}\right)d\vec{\xi}\,. \tag{3.1}$$

Let $f = \dfrac{\sum v_k}{V}$ be the volume fraction of the inclusion. We then have

$$\left\langle \vec{E}(\vec{x}) \right\rangle = (1-f)\left\langle \vec{E}_m(\vec{x}) \right\rangle + f\sum_k \omega_k \left\langle \vec{E}_k(\vec{x}) \right\rangle, \tag{3.2}$$

where $\omega_k = \frac{f_k}{f}$ and $\langle \vec{E}_k \rangle$ and $\langle \vec{E}_m \rangle$ are the average of the electric fields in the inclusion and host, respectively.

Similarly, the average polarization can be written as

$$\langle \vec{P}(\vec{x}) \rangle = (1-f)\langle \vec{P}_m(\vec{x}) \rangle + f\sum_k \omega_k \langle \vec{P}_k(\vec{x}) \rangle. \tag{3.3}$$

Assuming linear response as follows:

$$\langle \vec{P}_m(\vec{x}) \rangle = \varepsilon_m \cdot \langle \vec{E}_m(\vec{x}) \rangle, \tag{3.4}$$

$$\langle \vec{P}_k(\vec{x}) \rangle = \varepsilon \cdot \langle \vec{E}_k(\vec{x}) \rangle, \tag{3.5}$$

$$\langle \vec{P}(\vec{x}) \rangle = \varepsilon_{ave} \cdot \langle \vec{E}(\vec{x}) \rangle. \tag{3.6}$$

Substitute back to (3.3) and use (3.2), we have

$$(1-f)(\varepsilon_{ave} - \varepsilon_m)\langle \vec{E}_m(\vec{x}) \rangle + \varepsilon f \sum_k \omega_k \langle \vec{E}_k(\vec{x}) \rangle = 0. \tag{3.7}$$

For an isolated ellipsoid in a uniformed field $\vec{E}_m$, we can follow the approach of Bohren and Huffmann[21], assuming

$$\langle \vec{E}_k \rangle = \lambda_k \langle \vec{E}_m \rangle, \tag{3.9}$$

we finally get from (3.7):

$$\varepsilon_{ave} = \frac{(1-f)\varepsilon_m + \sum f_j \beta_j \varepsilon_j}{1-f+\sum f_j \beta_j}, \tag{3.10}$$

where β_j is the depolarizing field factor. For the case of a spherical particle

$$\beta_j = \frac{\varepsilon_j - \varepsilon_m}{\varepsilon_j + 2\varepsilon_m} \tag{3.11}$$

The final result for a system of identical spherical particles is then obtained as

$$\varepsilon_{ave} = \varepsilon_m \left(1 + \frac{3f\beta}{1-f\beta}\right). \tag{3.12}$$

FRACTAL CLUSTER MODEL

For the case when the particles coalesce to form local clusters, we have followed the differential effective medium formalism by Hui and Stroud [22] for the optical properties of fractal clusters. For a three dimensional (3D) fractal cluster, let ε_1 be the dielectric function of the host medium, $\varepsilon(a)$ be that of the spherical particles (of radius a) in the host medium, the effective dielectric function for this cluster $\varepsilon(R)$ can be obtained according to Hui and Stroud from the following expression:

$$\frac{\varepsilon(R)}{\varepsilon(a)}\left[\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 - \varepsilon(R)}\right]^3 = f', \tag{3.13}$$

where f' is the volume fraction of the particles in the cluster, given by

$$f' = \left[\frac{R}{a}\right]^{\beta(3-d_f)}, \qquad (3.14)$$

with d_f being the fractal dimension of the cluster. The dielectric function of the system which contains many such clusters is ultimately obtained by the application of the MG theory treating the system as a composite of these clusters (of low concentration c) and the host medium [22]. Note that for a given amount of total particle concentration of volume fraction V_f in the host material, we have $V_f = c \cdot f$, where c is concentration of coalesced clusters and f is the metallic volume fraction of each single cluster. Since this approach is limited to low particle concentrations, we shall compare our results with those obtained previously from the MG theory [15] for the case in which no clustering occurs.

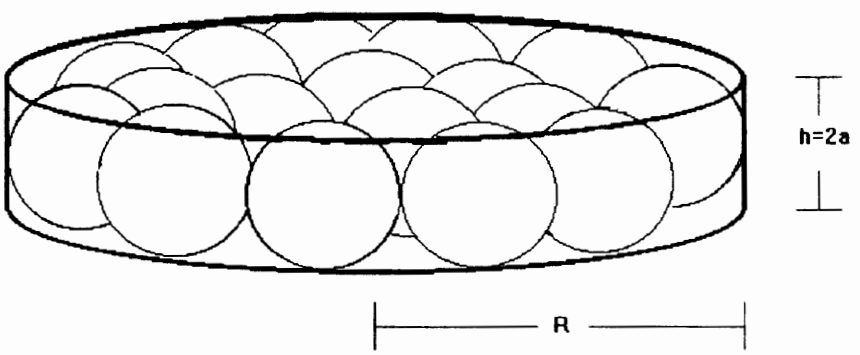

Fig. 6 2-D cluster.

However, to apply the approach of Hui & Stroud to model a fractal-clustered island film as described above, we must vary the original formulation to some extent that it

can model 2D clustering phenomenon. Consider a cluster with the radius of R and height of $h = 2a$ (a is the diameter of the particle) as shown in *Fig 6*, with the volume fraction of the metal $f(R)$ and $1 - f(R)$ for the host, respectively. Note that the cluster is cylindrical but the particles are of spherical shape. Assuming an infinitesimal increment of the radius δR of cluster, and let R', V' be the radius and volume of the enlarged cluster. (See *Fig. 7*).

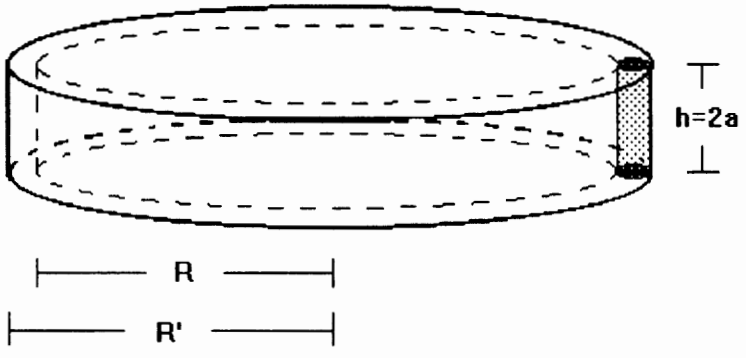

Fig. 7 The small "cylinder" of the insulator added.

We have,

$$f'(R) = \frac{df(R)}{dR},$$

$$R' = R + \delta R,$$

$$V' = A(R + \delta R)^2,$$

$$M' = \rho f(R+\delta R)V', \tag{3.15}$$

where M' is the mass of metal in the enlarged cluster with ρ the mass density of metal, and A is a constant ($2\pi h$ for a cylinder). To the first order of δR,

$$\delta V = 2AR\delta R,$$

$$\delta M = \rho\left[f(R)\delta V + V\delta f(R)\right],$$

$$\delta M = \rho\left[2AR\delta R f(R) + AR^2 f'(R)\delta R\right]. \tag{3.16}$$

Now we divide δV into two parts: δV_1 and δV_2, each represents the added metal and insulator, respectively. For δV, we assume that it has the same concentration $f(R)$ as the cluster to which it is being added:

$$\frac{\delta M_1}{\delta V_1} = \rho f(R) = \frac{\rho}{\delta V_1}\left[2AR\delta R f(R) + AR^2 f'(R)\delta R\right], \tag{3.17}$$

$$\delta V_1 = 2ARf(R)\delta R + AR^2\frac{f'(R)}{f(R)}\delta R = \delta V - \delta V_2. \tag{3.18}$$

Then δV_2 can be easily obtained,

$$\delta V_2 = -AR^2\frac{f'(R)}{f(R)}\delta R. \tag{3.19}$$

The volume fraction of the added insulator is

$$\eta \equiv \frac{\delta V_2}{V'}, \tag{3.20}$$

$$\eta = -\frac{f'(R)}{f(R)} \frac{R^2 \delta R}{(R+\delta R)^2}. \tag{3.21}$$

Take the first order of δR, we have,

$$\eta = -\frac{f'(R)}{f(R)} \delta R \tag{3.22}$$

In this situation, we can regard the increase in the insulator in the form of a small cylinder with diameter δR and the height of $h = 2a$, the diameter of the particle. (See *Fig. 7*). For a uniform external field $\vec{E}_0$ applied to a long dielectric cylinder, it can be shown that the field inside the cylinder is expressible as [23]:

$$\vec{E} = \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon} \vec{E}_0 \tag{3.23}$$

Applying this result to the MG approach of finding the effective dielectric function of a small volume fraction of cylinders, we obtain (cf Eqn. (3.12))

$$\varepsilon_{effective} - \varepsilon_0 = \eta \frac{2\varepsilon_0}{\varepsilon_0 + \varepsilon} (\varepsilon - \varepsilon_0) \tag{3.24}$$

Hence, we can apply this result to obtain a differential change for $\varepsilon(R)$ as follows:

$$\varepsilon(R+\delta R) - \varepsilon(R) = 2\eta\varepsilon(R) \frac{\varepsilon_1 - \varepsilon(R)}{\varepsilon_1 + \varepsilon(R)} \tag{3.25}$$

Substituting η and upon integration:

$$\int \frac{\varepsilon_1 + \varepsilon(R)}{\varepsilon_1 - \varepsilon(R)} \frac{d\varepsilon(R)}{\varepsilon(R)} = -2\int \frac{f'(R)}{f(R)} dR, \tag{3.26}$$

we obtain:

$$\frac{d\varepsilon}{dR} = -2\frac{f'(R)}{f(R)}\varepsilon(R)\frac{\varepsilon_1 - \varepsilon(R)}{\varepsilon_1 + \varepsilon(R)}. \tag{3.27}$$

Let $\varepsilon(R) = x$, we have

$$\int \frac{\varepsilon_1 + x}{\varepsilon_1 - x} \frac{dx}{x} = -2\int \frac{f'(R)}{f(R)} dR, \tag{3.28}$$

$$\Rightarrow \quad -2\ln\left[\varepsilon_1 - x\right] + \ln x \Big|_{\varepsilon(a)}^{\varepsilon(R)} = -2\ln f(R),$$

$$\Rightarrow \quad \ln\frac{\varepsilon(R)}{\left[\varepsilon_1 - \varepsilon(R)\right]^2} - \ln\frac{\varepsilon(a)}{\left[\varepsilon_1 - \varepsilon(a)\right]^2} = \ln\frac{1}{f^2(R)},$$

$$\Rightarrow \quad \frac{\varepsilon(R)}{\varepsilon(a)}\left[\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 + \varepsilon(R)}\right]^2 = \frac{1}{f^2(R)},$$

$$\Rightarrow \quad \left[\frac{\varepsilon(a)}{f^2(R)}\right]\varepsilon^2(R) - \left\{\left[\varepsilon_1 - \varepsilon(a)\right]^2 + 2\frac{\varepsilon_1\varepsilon(a)}{f^2(R)}\right\}\varepsilon(R) + \frac{\varepsilon_1^2\varepsilon(R)}{f^2(R)} = 0. \tag{3.29}$$

Solving the quadratic equation we obtain

$$\varepsilon(R) = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \tag{3.30}$$

$$\begin{aligned} A &= \frac{\varepsilon(a)}{f^2(R)} \\ B &= \left[\varepsilon_1 - \varepsilon(a)\right]^2 + 2\frac{\varepsilon_1 \varepsilon(a)}{f^2(R)} \\ C &= \frac{\varepsilon_1^2 \varepsilon(a)}{f^2(R)} \end{aligned} \tag{3.31}$$

Here we have two roots from the quadratic equation and only one is physically correct. We determine the correct result by requiring $\mathrm{Im}[\varepsilon(R)] > 0$, which corresponds to absorption of the incident fields.

Since we have cylindrical fractal cluster formed throughout the whole layer (*Region 2*) as illustrated in *Fig. 8*, we have to apply the effective medium theory again to calculate the average of the dielectric function of the layer.

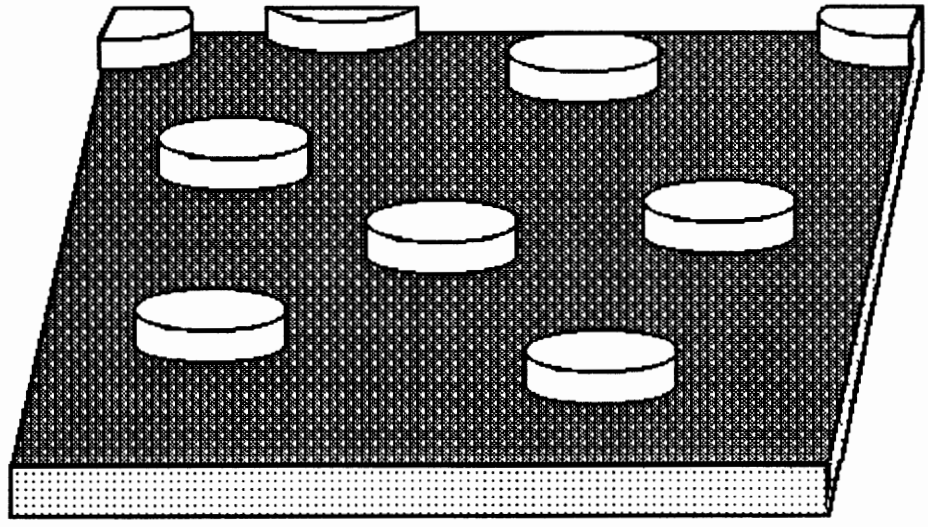

Fig 8. The 2D clusters on the interface.

By applying the MG method, we have (cf *Eqn. 3.10*):

$$\bar{\varepsilon} = \varepsilon_{medium}\left[1+\frac{f_v\beta\left(\varepsilon_{island}-\varepsilon_{medium}\right)}{\varepsilon_{medium}\left(1-f_v+f_v\beta\right)}\right] \tag{3.32}$$

where $\bar{\varepsilon}$ is the average dielectric function of the layer and f_v is the volume fraction of the clusters on the surface: $f_v = \frac{f}{f_c}$, where f_c.is the volume fraction within a single cluster.

In our case $\varepsilon_{medium} = \varepsilon_1$ and $\varepsilon_{cluster} = \varepsilon_2$ and is the solution from Eqn. (3.30).

For cylindrical particles

$$\beta = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}. \tag{3.33}$$

So we have

$$\bar{\varepsilon} = \varepsilon_1 \left[1 + \frac{2 f_v \beta_c}{1 - f_v \beta_c} \right] \tag{3.34}$$

where $\beta_c = \dfrac{\varepsilon(R) - \varepsilon_1}{\varepsilon(R) + \varepsilon_1}$ is the depolarizing field factor of the 2-D cluster. Hence the overall effective dielectric function for the roughened layer modeled as fractal-clustered spherical islands is given by Eqn. (3.34) [24].

CHAPTER IV

NUMERICAL RESULTS AND DISCUSSION

In **Chapter II** and **Chapter III** we have discussed the theoretical modeling of the molecular fluorescence near a roughened interface using both MG and FC theories. In this chapter we will perform some computational simulation based on those approaches. The results will also be discussed in this chapter.

The mechanism is shown in *Fig. 3,* **Chapter II**. The computation is based on Eqn.(2.36). Thus we have the molecule emitting at a wavelength of 3800Å in a medium with $\varepsilon = 1.5$ and the substrate is taken to be silver throughout, with the optical constants for silver($n=3.45$, $k=2.50$) available form the literature [25]. Also, applying the diffusion limited approximation (DLA) for a 3D self-developing cluster, the fractal dimension is *1.75*, and for the 2D case, it is *1.40*.

Fig. 9 shows the results for the normalized decay rates versus molecule-surface distances (*d*) for different values of the surface island radius in both the MG and the FC models. In the FC model, the particles (with radius 5, 10, and 20A) form clusters that are 10 times the size of the particles. The concentration of the particles is 1%, as the effective medium theory can only be correct in such low concentrations. It is clear that the case when the islands clustered will lead to a diminution of the induced decay rates as compared to the case when they disperse throughout the interface layer. Furthermore, whiled almost all the results obtained in this calculation within the range of the set of

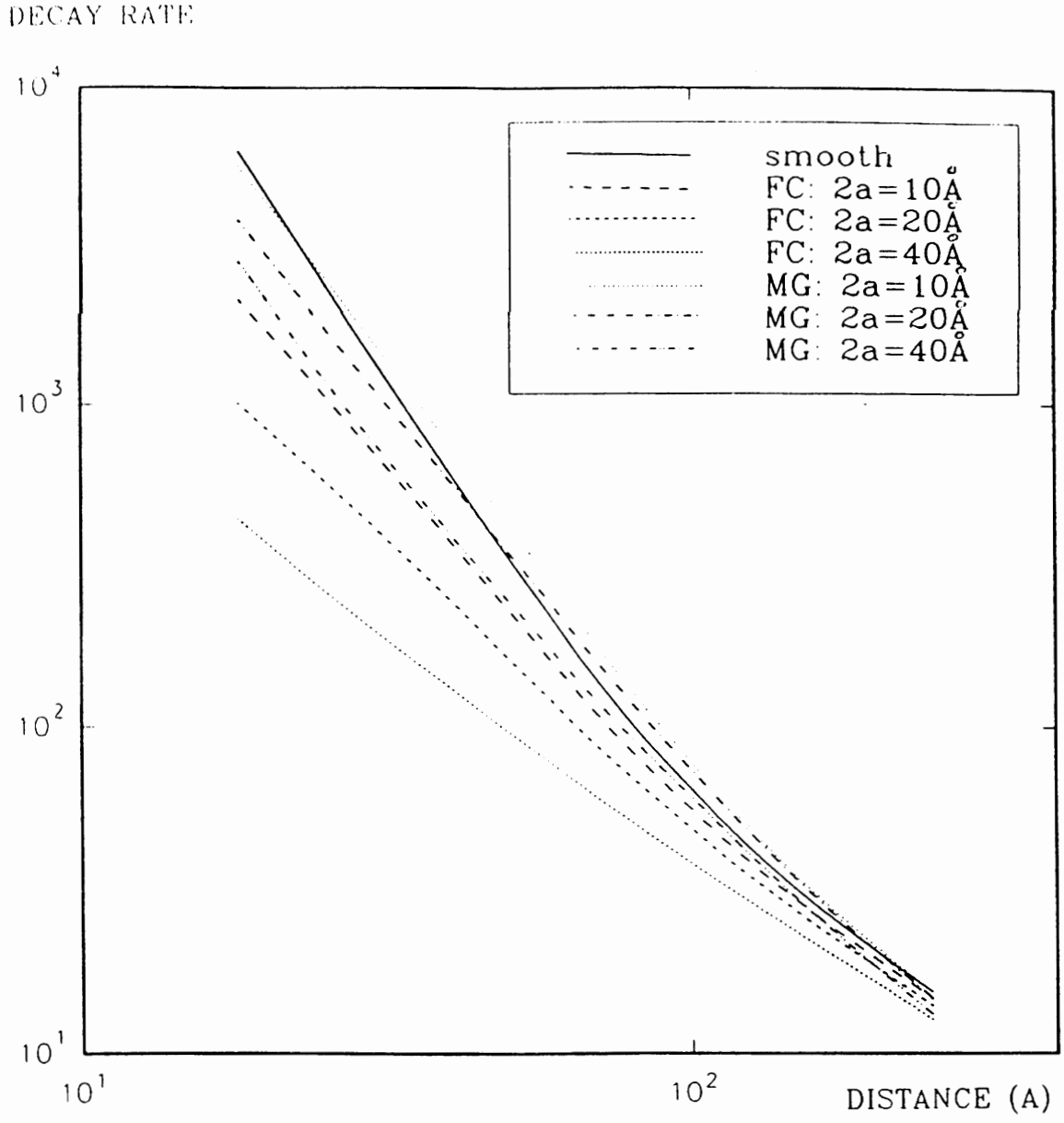

Fig. 9 Decay rates vs. molecule-surface distances. Particle's size varies from 5, 10 to 20A.

parameters are smaller than that for the flat surface case, "crossing" does occur between the flat surface and the MG curves. It can also occur with the FC curves for other set of parameters (see below). Thus it confirms once again hat the presence of surface roughness can lead to *both* possibilities of enhancing or suppressing the induced-decay rates for the admolecules as observed in various modeling works [8, 10, 12]. It is also remarkable to see the significant effects due to surface roughness at such close distances even for the slight presence of roughness at the interface (only 1% in volume fraction in this case). Comparison between the two models leads to the conclusion that the coalescence of the particles will cause a decrease in the decay rate.

Fig. 10 shows similar decay-rate plots (versus d) in the FC model for different values of the volume fraction of the islands. While suppression form the flat surface values is seen once again, it is comprehensible to see that as the "amount of metal" increases in the interfacial layer, dissipation leads to larger nonradiative decay and hence less suppression. Crossing between the FC and the flat curves finally take place for V_f roughly above 5%. We also performed a similar calculations with the MG model and find that just like the case in *Fig. 9*, most results are greater than those from the FC modeling and crossing with the flat surface curve occurs at a very low value of volume fraction at roughly above 0.5%.

Fig. 11 and *Fig. 12* show again similar plots with the FC fractal dimension varied. This shows qualitatively the effect due to different "degree of clustering" among the islands. When the particles coalesce to form clusters, the fractal dimension is a dominant parameter. However, we see that while the overall results are not very sensitive to this factor, surface-induced damping does increase with the fractal dimension and beyond a certain critical value of d_f (~1.8), the FC results become greater than those from the MG

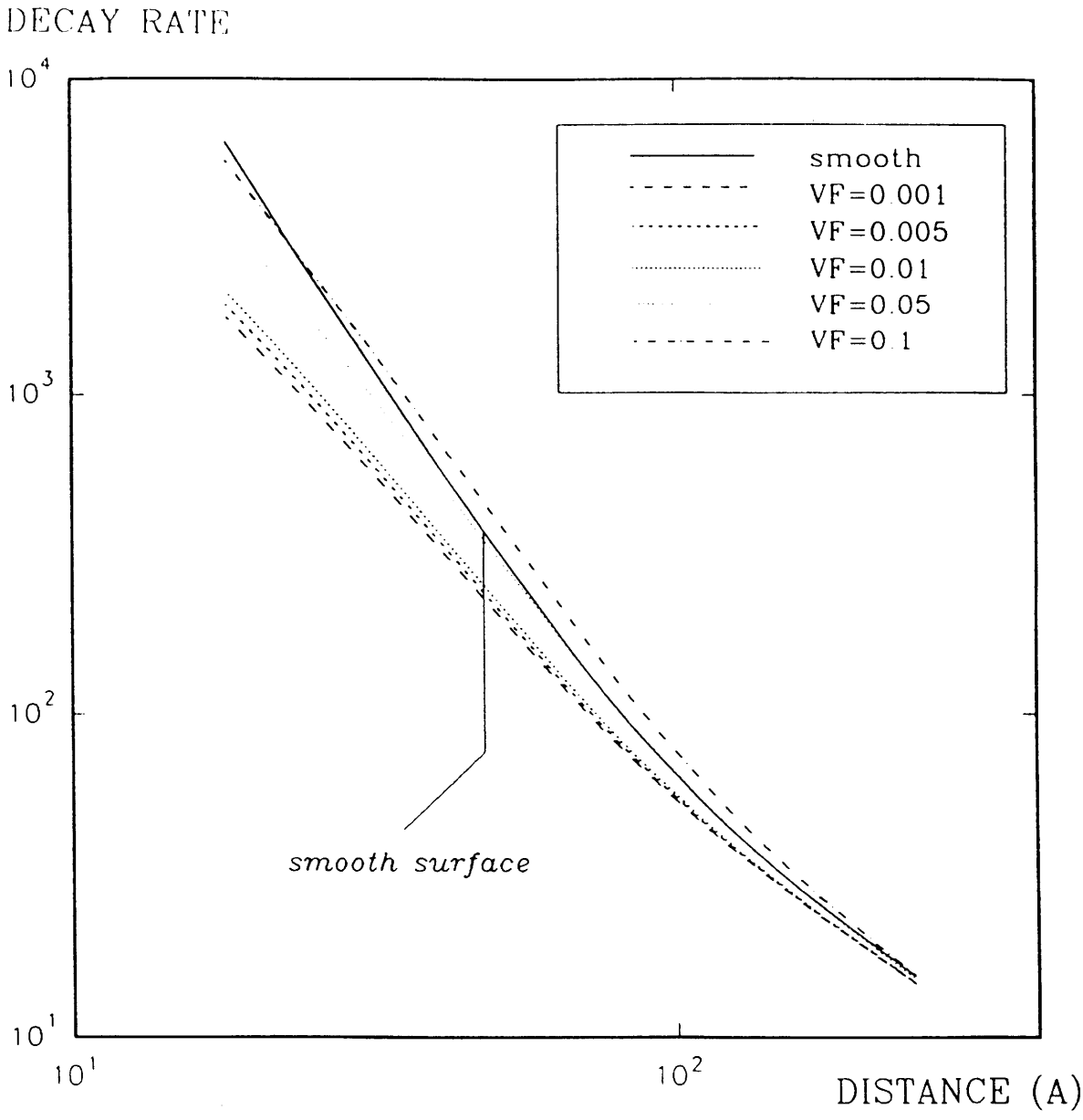

Fig. 10 Decay rates vs. molecule-surface distances. Volume fraction varies from 0.001 to 0.1

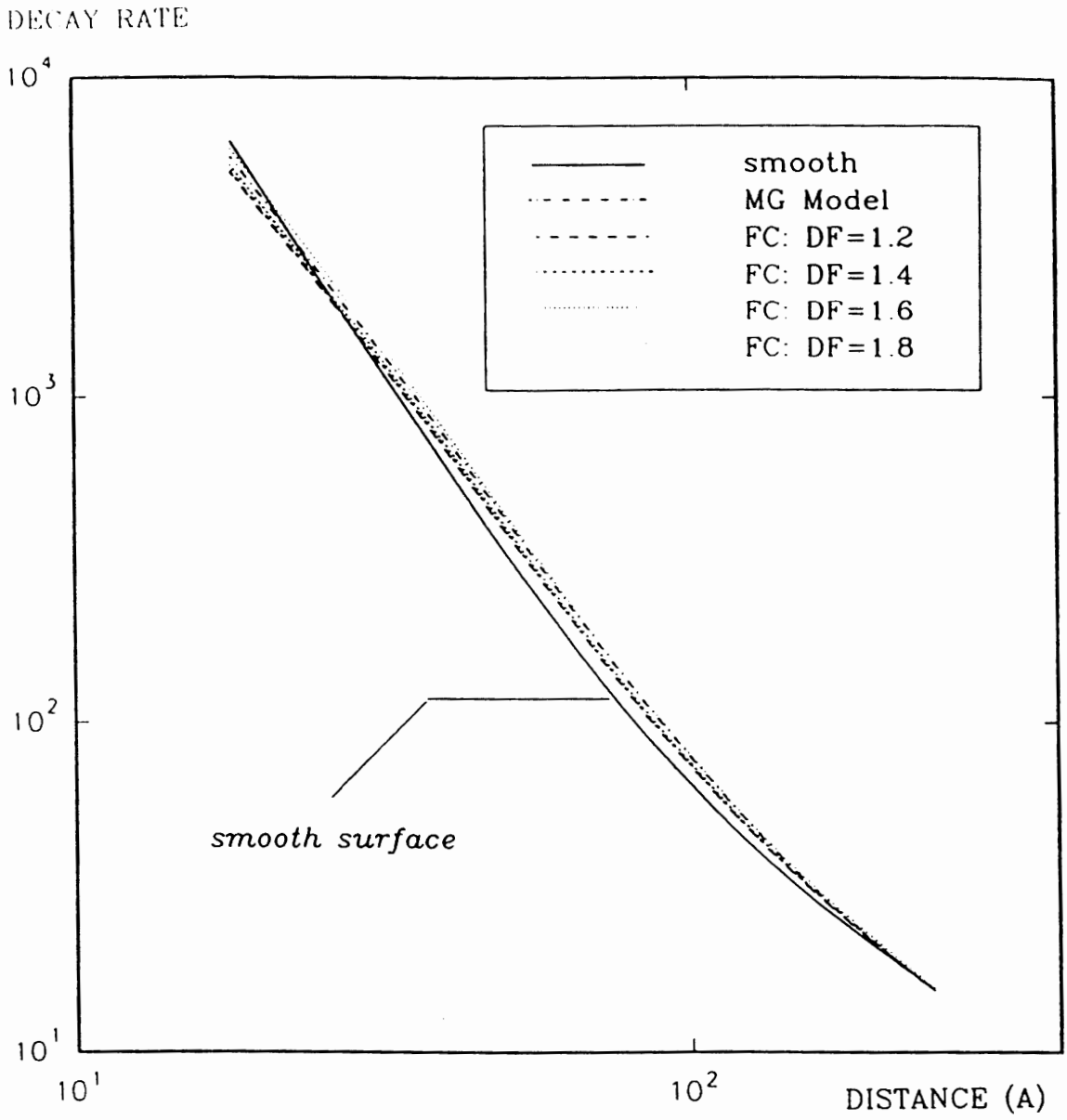

Fig. 11 Decay rates vs. molecule-surface distances. Fractal dimension varies from 1.2 to 1.8.

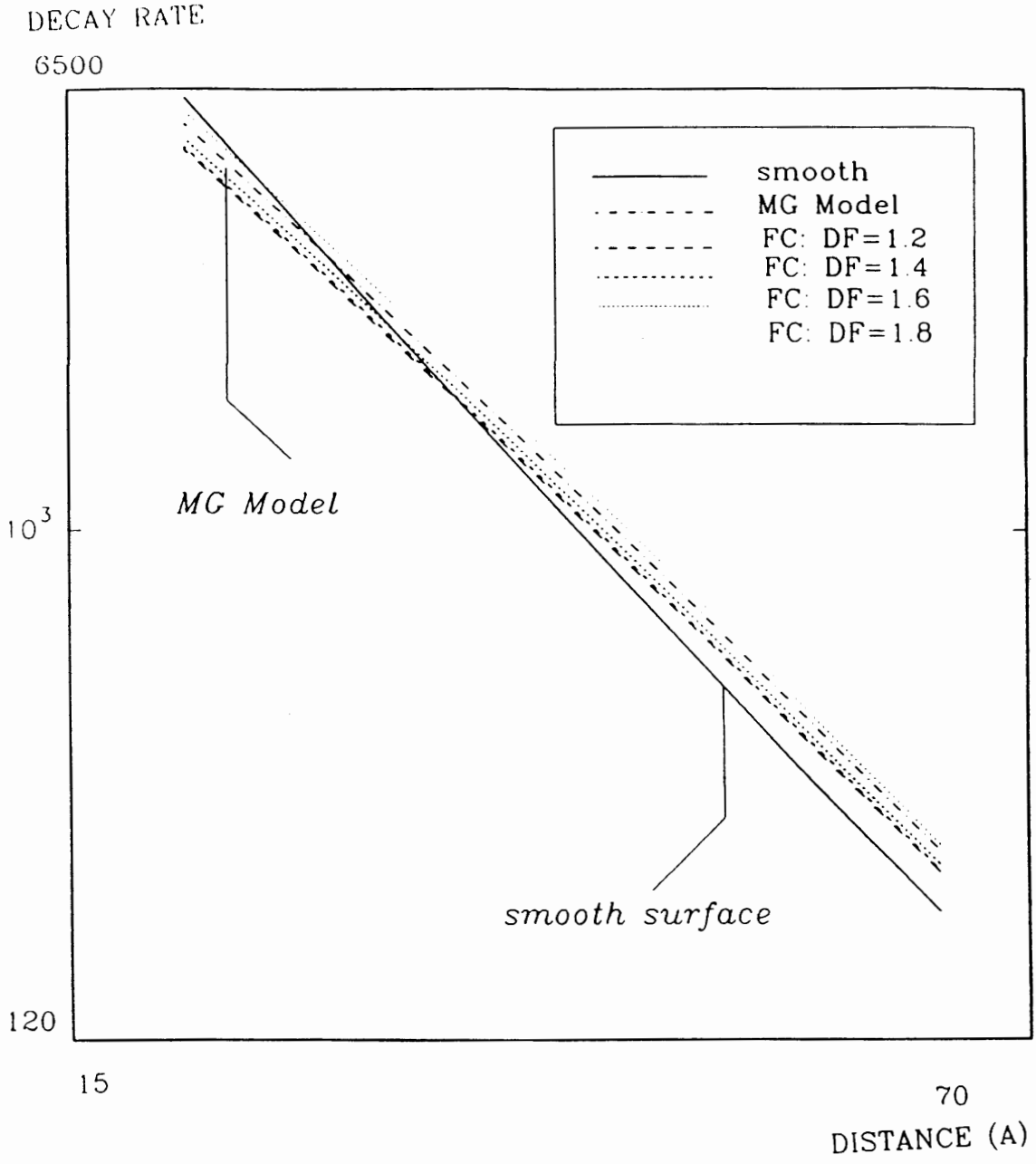

Fig. 12 Decay rates vs. molecule-surface distances. Zooming Fig. 11 in 15 to 75 molecule-surface distance. Fractal dimension varies from 1.2 to 1.8.

modeling. *Fig. 12*, which is a part of *Fig. 11*, is zooming to the range of the distance from 20 to 65 Å. The flat-surface curve crosses all the MG and FC lines at the range of about 20 to 30 Å. This means that surface roughness will suppress the surface-induced decay rates in the case irrespect to the degree of clustering of the surface islands at such close molecule-surface distances. We should also mention that aside from being insensitive to the parameter d in the FC model, the results are also completely insensitive to the cluster size. We have varied R/a from 5 to 50 and seen no appreciable change in the results. All these show that the degree of roughness (represented of the particles)is the most significant factor.

Fig. 13 shows a plot of induced decay rates versus emission frequency of the molecule for a distance fixed at d=50 Å. The other parameters are the same: 1% for concentration, 10A for particles size, 10 for R/a , and 1.4 for the cluster fractal dimension. We see that while the different cases (flat, MG, FC) give slightly deferent values for the decay rates, the resonant positions are almost identical and are all at roughly the flat-surface plasmon resonance frequency for silver (~3.5 eV). This is consistent with previous results obtained by modeling the island surface as a periodic 2D array of spheres in which it was hound that the nonradiative decay rates are quite insensitive to the geometrical structure of the substrate islands [13]. This is so for out calculation since at such a close distance of 50 Å, we expect that the total decay rate is mainly nonradidative in nature.

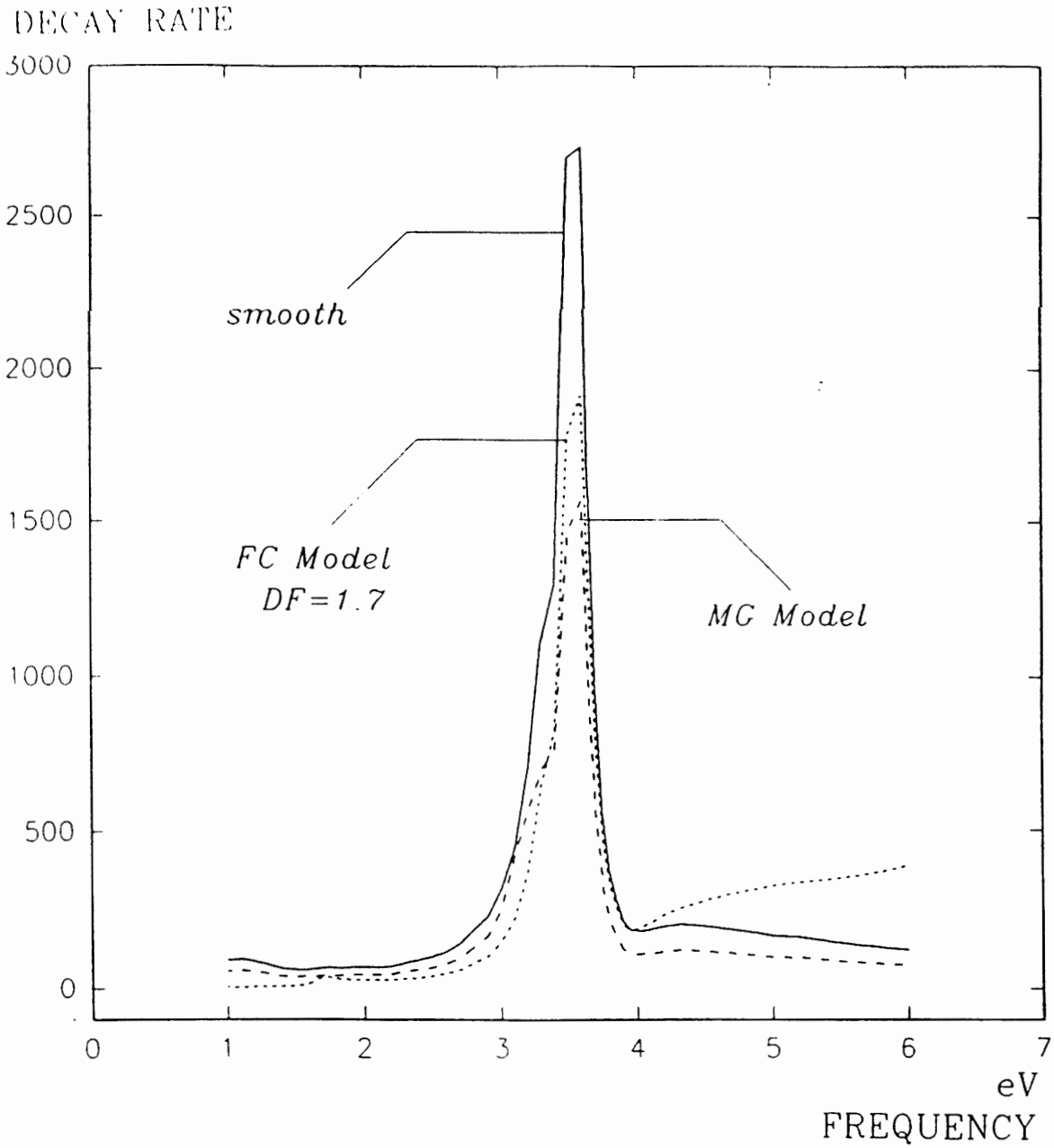

Fig. 13 Decay rates vs. emission frequency. Frequency ranges from 1 to 7 eV.

CHAPTER V

CONCLUSION

Within the mean field theory approach, we have studied the effect of surface roughness on the decay rates for admolecules in the vicinity of an island surface, paying particular attention to the role of the distribution of roughness at the interface. We believe that our modeling results can be tested since as mentioned above, fractal-clustering behavior among the islands was indeed observed in metal-on-metal growth processes. In comparison with previous modeling work which treats the surface islands as individual particles without averaging them over interfacial layer, our approach is highly simplified but limited in the sense that we cannot model the situation where the admolecule falls within the so-called "cavity site" at the interface. Moreover, our approach allows us to study different configurations for the distribution of the surface islands which would be otherwise extremely difficult without resorting to an all-numeric approach via computer simulation. Furthermore, as we have seen, the results obtained within this simple approach are quite consistent with previous results such as the possibility of both enhancing and suppressing flat-surface-induced decay rates due to the presence of roughness, as well as the insensitivity of the decay rates to the details of the island configuration at close molecule-surface distances.

REFERENCES

[1] R. R. Chance, A. Prock, and R. Silbey, *Adv. Chem. Phys.* **1978**, 37, 1 .

[2] A. Sommerfeld, *Ann. Phys.* (Leipzig), **1909**, 28, 665 ; **1926**, 81, 1135 ; "*Partial Differential Equations of Physics*", (Academic, New York, **1949**).

[3] K. H. Drexhage in *"Progress in Optics" XII*, E. Wolf, Ed., p. 195, (North Holland, Amsterdam, **1974**).

[4] H. Kuhn, *J. Chem. Phys.*, **1970**, 53, 101, and references therein.

[5] Alivisatos, A. P.; Waldeck, D. H.;Harris, C. B. *J. Chem. Phys.* **1985**, 83, 451.

[6] Persso, B. N. J.; Lang, N. D. *Phys. Rev. B* **1982**, 26, 5409.

[7] W. H. Weber and G. W. Ford, *Phys. Rev. Lett.*, **1980**, 44, 1774.

[8] P. T. Leung, *Phys. Rev. B.* **1990,** 42, 7622; P. T. Leung and M. H. Hider, *J. Chem. Phys.*, **1993,** 98, 5019

[9] J. Arias, P. K. Aravind and H. Metiu, *Chem. Phys. Lett.* **1982,** 85, 404 .

[10] P. T. Leung and T. F. George, *Phys. Rev. B.* **1987,** 36, 4664.

[11]. M. F. Ahmadi and J. F. Rusling, Langmuir, **1991**, 7, 1529.

[12] Y. S. Kim, P. T. Leung and T. F. George, *Surf. Sci.*, **1988**, 195, 1

[13] N. Liver , A. Nitzan, and K. F. Freed, *J. Chem. Phys.*, **1985**, 82, 3831 .

[14] J. C. Maxwell_Garnett, Philos. *Trans. R. Soc. London Ser.* **1904**, A 203, 385; **1906**, 205, 237.

[15] X. S. Li, D. L. Lin, and T. F. George, *Phys. Rev.* **1990,** B 41, 8107.

[16] X. S. Li, D. L. Lin, and T. F. George, Y. Liu, and Q. Gou, *Phys. Lett.*, **A 1990**, 145, 444.

[17] G. J. Kovacs and G. D. Scott, Phys. Rev., **1977,** B 16, 1297.

[18] D. Pines, D. Huppert, and D. Avnir, *J. Chem. Phys.*, **1988,** 89, 1177.

[19] See, e.g., Z. Zhang, X. Chen, and M. G. Lagally, *Phys. Rev. Lett.*, **1994** 73, 1829, and references therein.

[20] M. J. Pliska, E. J. Sanchez, P. T. Leung and T. F. George, *Solid State Comm.* , **1994**, 89, 397.

[21] C. F. Bohren and D. R. Huffman, *"Absorption and Scattering of Light by Small Particles"*, (Wiley, New York, **1983**).

[22] P. M. Hui and D. Stroud, *Phys. Rev.* **1986**, B 33, 2163; C. Y. Chang, L. C. Kuo, and P. M. Hui, *Phys. Rev.* **1992**, B 46, 14505.

[23] See, e. g, L. D. Landau, E. M. Lifshiz and L.P. Pitaevshii, "*Electrodynamicsof Continuous Media*", (Pergamon, Oxford, **1984**).

[24] P. T. Leung, D. Pollard-Knight, G. P. Malan, and M. F. Finlan, *Sensors and Actuators v:* **B 1994**, 22, 175.

[25] E. D. Palik ed., "*Handbook of Optical Constants of Solids*", (Academic, New York, **1985**).

APPENDIX A

COMPUTER PROGRAMS

```
c     This is a fortran program computes the decay rate of
fluorescing molecule
c     at  an interface of two different media.

      IMPLICIT REAL*8 (A-H,O-Z)
      COMPLEX*16 CI,E1,E2,E3,XE,ES2
      COMPLEX*16 COEA,COEB,COEC,EC1,EC2,BXE
      COMMON/COM/CI,WN,S1,S2,E1,E2,E3
      EXTERNAL F,dQDAGP
c 25  PRINT 30
c 30  FORMAT ( ' R/A,VF,DF,AFC ' )
c     READ*, SIZE,VF,DF,AFC
c     S2=2.D0*AFC
c     vf=0.2d0
C     do 1100 s1=0.01,0.42,0.01
      b=3000.d0
      A=0.0d0
      ER1=1.7d0
      EI1=0.0d0
      ER3=-3.16d0
      EI3=0.29d0
      E1=dCMPLX(ER1,EI1)
      E3=dCMPLX(ER3,EI3)
100   PRINT 110
110   FORMAT ( ' MODEL CHOICES: FC=1, MG=2 ' )
      READ*,I
      IF ( I .EQ. 2 ) GOTO 450
C     -----FC MODEL
140   print 150
150   format ( ' R/A,VF,DF,AFC ' )
      READ*, SIZE,VF,DF,AFC
      SS2=2.D0*AFC
      S2=SS2*2.D0*3.14159D0/3800.D0
      b=3000.
400   RA=SIZE
      PF=RA**(DF-2.D0)
      COEA=E3/PF**2
      COEB=(E1-E3)**2.D0+2.D0*E1*E3/PF**2.D0
      COEC=E3*(E1/PF)**2.D0
      EC1=(COEB+CDSQRT(COEB**2.D0-4.D0*COEA*COEC))/2.D0/COEA
```

```
      EC2=(COEB-CDSQRT(COEB**2.D0-4.D0*COEA*COEC))/2.D0/COEA
      ECI1=DIMAG(EC1)
      ECI2=DIMAG(EC2)
      IF ( ECI1 .gt. 0.0) GOTO 410
      IF ( ECI2 .gt. 0.0) GOTO 430
      PRINT 405
405   FORMAT ( ' WRONG! " )
      GOTO 7000
410   ES2=EC1
      GOTO 440
430   ES2=EC2
440   BXE=(ES2-E1)/(ES2+E1)
      VFF=VF/PF
      E2=E1*(1.D0+(2.D0*VFF*BXE)/(1.D0-VFF*BXE))
      GOTO 700
C     -----
C     -----MG MODEL
450   PRINT 500
500   FORMAT ( ' VF, THICKNESS ' )
      READ*, VF, SS2
      S2=SS2*2.D0*3.14159D0/3800.D0
      XE=VF*(E3-E1)/(E3+2.D0*E1)
      E2=E1*(1.D0+3.D0*XE/(1.D0-XE))
C 600 E2=E1*(E3*(1.+2.*VF)+2.*E1*(1.-VF))/(E3*(1.-
VF)+E1*(2.+VF))
C     -----
700   DO 1100 S1=0.03,0.42,0.01
      AA=0.d0
      BB=1.d0
      CI=dCMPLX(AA,BB)
      ERRABS=1.d-8
      ERRREL=1.d-8
      NPTS=1
      POINTS=1.0
      CALL
dQDAGP(F,A,B,NPTS,POINTS,ERRABS,ERRREL,RESULT1,ERREST)
      WN=2.*3.1415926/3800.d0
      DECAY=1.-1.5*RESULT1
      time=1./DECAY
      SS1=S1*3800./(2.*3.14159)
      PRINT*,SS1,DECAY
        write(7,*)ss1,decay
1100  continue
7000  STOP
      END
      FUNCTION F(U)
      implicit real*8 (a-h, o-z)
      COMPLEX*16
E1,E2,E3,CI,CL1,CL2,CL3,CR12,CR23,CEX1,CEX2,G
      COMMON/COM/CI,WN,S1,S2,E1,E2,E3
      CL1=-CI*CdSQRT(1.+CI*CI*U**2)
      CL2=-CI*CdSQRT(E2/E1-U**2)
```

```
      CL3=-CI*CdSQRT(E3/E1-U**2)
      CR12=(E1*CL2-E2*CL1)/(E1*CL2+E2*CL1)
      CR23=(E2*CL3-E3*CL2)/(E2*CL3+E3*CL2)
      CEX1=2.*CL1*S1
      CEX2=2.*CL2*S2
C      CEX1=2.*CL1*S1*WN
C      CEX2=2.*CL2*S2*WN
      G=(CR12+CR23*CdEXP(-CEX2))/(1.+CR12*CR23*CdEXP(-CEX2))
     &*CdEXP(-CEX1)*U*U*U/CL1
      F=dIMAG(G)
      RETURN
      END
```

```
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER (N=52)
      COMPLEX*16 CI,E1,E2,E3,XE,ES2
      COMPLEX*16 COEA,COEB,COEC,EC1,EC2,BXE
      COMMON/COM/CI,WN,S1,S2,E1,E2,E3
      REAL FR(N), RN(N), RK(N)
      EXTERNAL F,dQDAGP
      DATA ( FR(I), I=1,N
)/1.,1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,
     #  2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,
     #
3.,3.1,3.2,3.3,3.4,3.5,3.6,3.65,3.7,3.75,3.8,3.85,3.9,3.95,
     #  4.,4.05,4.1,4.15,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,
     #  5.0,5.2,5.4,5.6,5.8,6.0/
      DATA ( RN(I),
I=1,N)/.329,.251,.226,.198,.163,.145,.143,.148,
     #  .14,.14,
     #  .131,.121,.12,.129,.13,.13,.132,.144,.157,.16,
     #
.173,.173,.192,.2,.186,.209,.238,.259,.294,.371,.526,
     #  .708,.932,1.149
     #
1.323,1.432,1.496,1.522,1.519,1.502,1.476,1.441,1.404,1.372,
     #  1.343,1.320,
     #  1.298,1.265,1.238,1.208,1.173,1.125/
      DATA ( RK(I), I=1,N
)/8.49,7.67,6.99,6.43,5.95,5.5,5.09,4.74,
     #  4.44,4.15,
     #  3.88,3.66,3.45,3.25,3.07,2.88,2.72,2.56,2.4,2.26,
     #
2.11,1.95,1.81,1.67,1.61,1.44,1.24,1.12,.986,.813,.663,.565,
     #  .504,.540,
     #
.647,.766,.882,.992,1.08,1.19,1.26,1.31,1.33,1.35,1.35,1.35,
     #  1.35,1.33,1.31,1.3,1.29,1.27/
      b=3000.d0
      A=0.0d0
      ER1=1.7d0
      EI1=0.0d0
      E1=dCMPLX(ER1,EI1)
      PRINT 120
120   FORMAT ( ' S1 ' )
      READ*, S1
C     -----FC MODEL
140   print 150
150   format ( ' R/A,VF,DF,AFC ' )
      READ*, SIZE,VF,DF,AFC
      S2=2.D0*AFC
      DO 1100 J=1,52
      ER3=RN(J)*RN(J)-RK(J)*RK(J)
      EI3=2.D0*RN(J)*RK(J)
      b=3000.
```

```
400    RA=SIZE
       PF=RA**(DF-2.D0)
       COEA=E3/PF**2
       COEB=(E1-E3)**2.D0+2.D0*E1*E3/PF**2.D0
       COEC=E3*(E1/PF)**2.D0
       EC1=(COEB+CDSQRT(COEB**2.D0-4.D0*COEA*COEC))/2.D0/COEA
       EC2=(COEB-CDSQRT(COEB**2.D0-4.D0*COEA*COEC))/2.D0/COEA
       ECI1=DIMAG(EC1)
       ECI2=DIMAG(EC2)
       IF ( ECI1 .gt. 0.0) GOTO 410
       IF ( ECI2 .gt. 0.0) GOTO 430
       PRINT 405
405    FORMAT ( ' WRONG! " )
       GOTO 7000
410    ES2=EC1
       GOTO 440
430    ES2=EC2
440    BXE=(ES2-E1)/(ES2+E1)
       VFF=VF/PF
       E2=E1*(1.D0+(2.D0*VFF*BXE)/(1.D0-VFF*BXE))
       GOTO 700
       AA=0.d0
       BB=1.d0
       CI=dCMPLX(AA,BB)
       ERRABS=1.d-8
       ERRREL=1.d-8
       NPTS=1
       POINTS=1.0
       CALL
dQDAGP(F,A,B,NPTS,POINTS,ERRABS,ERRREL,RESULT1,ERREST)
       WN=2.*3.1415926/3800.d0
       DECAY=1.-1.5*RESULT1
       time=1./DECAY
       PRINT*,FR(J),DECAY
         write(7,*)FR(J),decay
1100   continue
7000   STOP
       END
       FUNCTION F(U)
       implicit real*8 (a-h, o-z)
       COMPLEX*16
E1,E2,E3,CI,CL1,CL2,CL3,CR12,CR23,CEX1,CEX2,G
       COMMON/COM/CI,WN,S1,S2,E1,E2,E3
       CL1=-CI*CdSQRT(1.+CI*CI*U**2)
       CL2=-CI*CdSQRT(E2/E1-U**2)
       CL3=-CI*CdSQRT(E3/E1-U**2)
       CR12=(E1*CL2-E2*CL1)/(E1*CL2+E2*CL1)
       CR23=(E2*CL3-E3*CL2)/(E2*CL3+E3*CL2)
C       CEX1=2.*CL1*S1
C       CEX2=2.*CL2*S2
       CEX1=2.*CL1*S1*WN
       CEX2=2.*CL2*S2*WN
```

```
 G=(CR12+CR23*CdEXP(-CEX2))/(1.+CR12*CR23*CdEXP(-CEX2))
&*CdEXP(-CEX1)*U*U*U/CL1
 F=dIMAG(G)
 RETURN
 END
```

```
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER (N=52)
      COMPLEX*16 CI,E1,E2,E3,XE,ES2
      COMPLEX*16 COEA,COEB,COEC,EC1,EC2,BXE
      COMMON/COM/CI,WN,S1,S2,E1,E2,E3
      REAL FR(N), RN(N), RK(N)
      EXTERNAL F,dQDAGP
      DATA ( FR(I), I=1,N
)/1.,1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,
     #  2.0,2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,
     #
3.,3.1,3.2,3.3,3.4,3.5,3.6,3.65,3.7,3.75,3.8,3.85,3.9,3.95,
     #  4.,4.05,4.1,4.15,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,
     #  5.0,5.2,5.4,5.6,5.8,6.0/
      DATA ( RN(I),
I=1,N)/.329,.251,.226,.198,.163,.145,.143,.148,
     #  .14,.14,
     #  .131,.121,.12,.129,.13,.13,.132,.144,.157,.16,
     #
.173,.173,.192,.2,.186,.209,.238,.259,.294,.371,.526,
     #  .708,.932,1.149
     #
1.323,1.432,1.496,1.522,1.519,1.502,1.476,1.441,1.404,1.372,
     #  1.343,1.320,
     #  1.298,1.265,1.238,1.208,1.173,1.125/
      DATA ( RK(I), I=1,N
)/8.49,7.67,6.99,6.43,5.95,5.5,5.09,4.74,
     #  4.44,4.15,
     #  3.88,3.66,3.45,3.25,3.07,2.88,2.72,2.56,2.4,2.26,
     #
2.11,1.95,1.81,1.67,1.61,1.44,1.24,1.12,.986,.813,.663,.565,
     #  .504,.540,
     #
.647,.766,.882,.992,1.08,1.19,1.26,1.31,1.33,1.35,1.35,1.35,
     #  1.35,1.33,1.31,1.3,1.29,1.27/
      b=3000.d0
      A=0.0d0
      ER1=1.7d0
      EI1=0.0d0
C     -----MG MODEL
      PRINT 200
200   FOMAT ( ' S1 ' )
      READ*, S1
450   PRINT 500
500   FORMAT ( ' VF, THICKNESS ' )
      READ*, VF, S2
      DO 1100 J=1, 52
      ER3=RN(J)**2.D0-RK(J)**2.DO
      EI3=2.D0*RN(J)*RK(J)
      E3=dCMPLX(ER3,EI3)
      XE=VF*(E3-E1)/(E3+2.D0*E1)
      E2=E1*(1.D0+3.D0*XE/(1.D0-XE))
```

```
C 600 E2=E1*(E3*(1.+2.*VF)+2.*E1*(1.-VF))/(E3*(1.-
VF)+E1*(2.+VF))
      AA=0.d0
      BB=1.d0
      CI=dCMPLX(AA,BB)
      ERRABS=1.d-8
      ERRREL=1.d-8
      NPTS=1
      POINTS=1.0
      CALL
dQDAGP(F,A,B,NPTS,POINTS,ERRABS,ERRREL,RESULT1,ERREST)
      WN=2.*3.1415926/3800.d0
      DECAY=1.-1.5*RESULT1
      time=1./DECAY
      PRINT*,FR(J),DECAY
        write(7,*)FR(J),decay
1100  continue
7000  STOP
      END
      FUNCTION F(U)
      implicit real*8 (a-h, o-z)
      COMPLEX*16
E1,E2,E3,CI,CL1,CL2,CL3,CR12,CR23,CEX1,CEX2,G
      COMMON/COM/CI,WN,S1,S2,E1,E2,E3
      CL1=-CI*CdSQRT(1.+CI*CI*U**2)
      CL2=-CI*CdSQRT(E2/E1-U**2)
      CL3=-CI*CdSQRT(E3/E1-U**2)
      CR12=(E1*CL2-E2*CL1)/(E1*CL2+E2*CL1)
      CR23=(E2*CL3-E3*CL2)/(E2*CL3+E3*CL2)
C      CEX1=2.*CL1*S1
C      CEX2=2.*CL2*S2
      CEX1=2.*CL1*S1*WN
      CEX2=2.*CL2*S2*WN
      G=(CR12+CR23*CdEXP(-CEX2))/(1.+CR12*CR23*CdEXP(-CEX2))
     &*CdEXP(-CEX1)*U*U*U/CL1
      F=dIMAG(G)
      RETURN
      END
```

APPENDIX B

PUBLICATION

Modeling of Decay Rates for Molecules at an Island Surface

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The decay rates for molecules at rough surfaces are studied via an island surface model, with particular emphasis on the effect due to the *distribution* of surface roughness. Two extreme cases are studied when the surface islands distribute themselves evenly and when they coalesce to form local clusters at the molecule-substrate interface. The optical properties of the interfacial layer in these two cases are described by the Maxwell-Garnett and the fractal-cluster models, respectively. Among other results, it is found that both enhancement and suppression of the surface-induced decay rates are possible due to the presence of roughness, with more dramatic suppression taking place when the surface islands coalesce to form clusters.

INTRODUCTION

The study of optical phenomena at rough interfaces has remained a topic of constant interest for over a hundred years. Among these, optical absorption and emission from adsorbed molecules have been studied intensively after the discovery of the dramatic surface enhancement of Raman scattering in 1974, for which roughness of the substrate metallic surface is understood to play the most significant role leading to the enhancement of the signal.[1] In particular, both experimental and theoretical studies of fluorescence from molecules at metal surfaces had been carried out in great detail by the late 1970's in the "far-distance regime" with molecule-surface distances (d) greater than about 100 Å. Among many theoretical descriptions, the phenomenological approach of Chance, Prock and Silbey (CPS) stood out as one of the simplest models which had been very successful in explaining the observed modified lifetimes and level-shifts for the admolecules fluorescing in the vicinity of a metal surface.[2] It was not until the early 80's when experiments were carried out in the close distance regime (d<100 Å) that the CPS theory was found inadequate.[3,4] Many theoretical propositions have then been put forward to explain the discrepancy observed in the data and thereby modifying the CPS theory. These include the effects due to surface damping,[4,5] surface roughness,[6,7] and the nonlocal dielectric response of the substrate,[8,9] among others.

While all these effects or different combinations among them are plausible for explaining the data observed in a particular "close-distance experiment", we shall address specifically the effects due to surface roughness in this present work. Previous works have already studied this problem by modeling the surface as both a randomly-(Gaussian-distributed)[6] or periodically-roughened substrate.[7] Among other results, it was pointed out that the presence of roughness could lead to a suppression of nonradiative decay and hence *enhancement* of fluorescence compared to the flat surface case, due to a re-coupling of the non-radiative surface plasmon to radiative modes.[7] A recent experiment performed by Ahmadi and Rusling[10] has indeed revealed the possibility of observing enhanced fluorescence from pyrene adsorbed at a rough silver electrode. Aside from "extended" surface morphologies, "localized" structures have also been considered in the literature with most of the works adopting the "island surface model". In particular, the cases of an isolated surface island[11,12] as well as a two-dimensional array of islands[13] have all been studied previously. While the single island case has been studied very thoroughly taking into consideration also the nonlocal dielectric response of the substrate,[9] the case for a "two-island" or "many-island" substrate usually becomes quite complicated mathematically. A previous treatment has been limited to a static theory with local dielectric reponse from the substrate and the islands modeled as a 2D square periodic array of interacting spheres.[13] Detailed numerical results of up to a "five-sphere" substrate were worked out, and it was found that the nonradiative decay rates are quite insensitive to the geometry of the clustering spheres as long as the molecule is not located in the "cavity-site" (i.e. the space between two islands). An alternative and simpler approach would be to apply mean-field theory to calculate an "effective" dielectric response for the two-dimensional island layer at the interface. To this end, the theories of Maxwell-Garnett[14,15] and Bruggemen[16] have often been applied.

These previous investigations have all assumed that

the distribution of the surface islands is uniform throughout the interface layer,[15,17] which may not be very realistic for certain kinds of interfaces. In fact, a recent experiment on the fluorescence of R6G and malachite on porous silica surfaces has revealed fractal nature for the substrate surface.[18] More recently, scanning tunneling microscopy studies of metal-on-metal growth at submonolayer coverages have also revealed formation of fractal-like islands at the interface.[19] Hence, it is of interest to go beyond the "uniform-distribution" assumption for the islands to model the interfacial roughness. It is the purpose of the present work to study the effect of the "distribution of roughness" at the interface on the decay rates of the admolecules. We shall look at the extreme case where the surface islands coalesce to form clusters and compare with the results in the other extreme where they disperse themselves uniformly throughout the interfacial layer.

THEORETICAL MODELING

For simplicity, we shall assume the admolecule to be a point dipole at a distance d from and oriented perpendicular to the substrate surface. The roughness at the interface is modeled as a 2D array of spherical islands (of equal radii a) with the distribution of these spheres being arbitrary. We shall apply below an effective medium theory to calculate an average dielectric function for this "island layer" of thickness 2a. Thus we have to solve the problem involving an emitting dipole on a "layered system" with the surface roughness now being replaced by a layer with an effective dielectric function (ε) calculated in terms of those of the molecular and of the substrate media. According to the phenomenological approach[2] and for a quantum yield of unity, the decay rate of the admolecule normalized to the free decay rate value can be expressed in the form

$$\frac{\gamma}{\gamma_0} = 1 - \frac{3}{2}\mathrm{Im}\int_0^{\infty} \mathrm{Re}^{-2l_1 k d_1}\frac{u^3}{l_1}\,du, \tag{1}$$

where $k = \sqrt{\varepsilon_1}\,\omega/c$ is the emission wave number of the molecule and $l_1 = -i\sqrt{1-u^2}$. R is a kind of Fresnel reflection coefficient given by

$$R = \frac{R_{12} + R_{23}e^{-2l_2 k d_2}}{1 + R_{12}R_{23}e^{-2l_2 k d_2}}, \tag{2}$$

with $R_{ij} = (\varepsilon_i l_j - \varepsilon_j l_i)/(\varepsilon_i l_j + \varepsilon_j l_i)$ and $l_2 = -i\sqrt{\varepsilon_2/\varepsilon_1 - u^2}$. ε_1 and ε_2 are the dielectric functions of the molecular and the substrate media, respectively, the distance d_1 is that from the molecule to the interface and $d_2 = 2a$ is the thickness of the layer.

In order to study the effect due to the distribution of roughness at the interface on the decay rates, we have adopted the two models below (labelled as A and B) for the calculation of ε in terms of ε_1 and ε_2. We shall limit ourselves to the case of weakly-roughened surfaces so that the concentrations of these surface islands are low.

Model A: Maxwell-Garnett Model

To model the case when the surface islands are dispersed uniformly throughout the layer, we follow the previous work[15,17] to adopt the Maxwell-Garnett (MG) model to determine the average dielectric function (ε) of the interfacial layer. The MG model is an effective medium theory which is accurate for small particle concentration. For spherical particles of dielectric function ε_2 distributed in a host medium ε_1, ε can be obtained as

$$\varepsilon = \varepsilon_1\left(1 + \frac{3f\beta}{1 - f\beta}\right), \tag{3}$$

where f is the volume fraction of the particles, and β is the depolarizing field factor which takes the following form for spherical particles:

$$\beta = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}, \tag{4}$$

Note that ε in this case does not explicitly depend on the radius of the sphere.

Model B: 2D Fractal Cluster Model

For the other extreme where the particles coalesce to form local clusters, we have adopted the differential effective medium formalism by Hui and Stroud for the optical properties of fractal clusters.[20] Despite the simplicity of this model, it has been found that the results so obtained agree quite well to a certain extent with those from a more accurate computer simulation approach.[21] To be applicable to our present situation with the islands at the interfacial layer, the original version of the fractal cluster (FC) model must be varied a little. Instead of forming three-dimensional (3D) fractal clusters as in Ref. 20, mainly 2D clusters are formed here when the islands coalesce at the interface.[22] We recapitulate here some results from Refs. 20 and 22 in order to make our presentation clear. Following Ref. 20, we assume at a certain instant during the formation of the 2D (cylindrical) cluster that the size has grown to a radius R (thickness 2a), with a dielectric function ε(R). Then, for an infinitesimal increment in the size of the cluster, one can apply the effective medium theory to obtain[22]

$$\varepsilon(R + dR) = \varepsilon(R) - 2\varepsilon(R)\frac{f_c'(R)}{f_c(R)}\frac{\varepsilon_1 - \varepsilon(R)}{\varepsilon_m + \varepsilon(R)}dR, \quad (5)$$

where $f_c(R) = df_c/dR$, with f_c being the volume fraction of the islands in the cluster, and for a 2D FC, we have

$$f_c(R) = \left(\frac{R}{a}\right)^{d_f - 2}, \quad (6)$$

with d_f (< 2) being the fractal dimension of the cluster. One can hence obtain a differential equation involving $\varepsilon(R)$ from Eq.(6) which, on integration, yields the following algebraic equation for $\varepsilon(R)$:

$$\frac{\varepsilon(R)}{\varepsilon(a)}\left[\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 - \varepsilon(R)}\right]^2 = [f_c(R)]^{-2}. \quad (7)$$

This result closely resembles that for the 3D cluster given in Ref. 20. Note that $\varepsilon(a) = \varepsilon_2$ and is simply the dielectric function of the islands and the substrate. We shall assume here a metallic substrate with a complex dielectric function. Solving Eq. (7) as a quadratic equation for $\varepsilon(R)$ and ignoring the solution with a negative imaginary part,[20] one can obtain a unique result for the dielectric function of *one* cluster of the spherical particles when they coalesce.

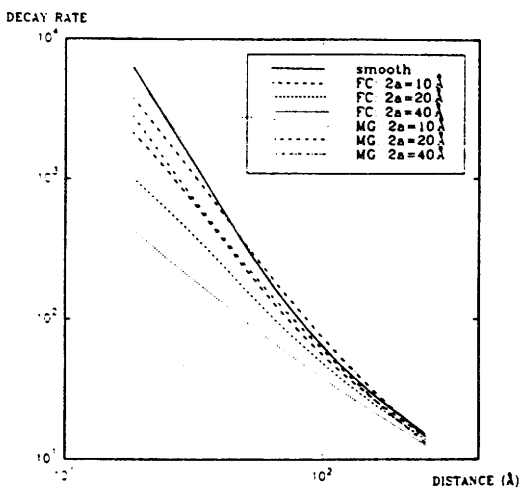

Fig. 1. Plot of normalized induced-decay rates versus molecular-surface distances for different sizes of the islands, with the interfacial roughened layer modeled according to both the Maxwell-Garnett (MG) and the fractal cluster (FC) models. The emission wavelength is fixed at 3800 Å, the volume fraction of the islands at 0.01, the fractal dimension at 1.7 for the FC case, and the size of one 2D cluster at R/a = 10.

The ultimate dielectric function for the whole "roughened layer" when the islands coalesce to form local fractal clusters is obtained by another application of the effective medium (MG) theory to a *collection of these 2D clusters*, as indicated briefly below.

Let $f_v = f/f_c$ be the volume fraction of these 2D clusters in the layer. The average dielectric function for the island layer in the clustering case can then be given by[14]

$$\varepsilon = \varepsilon_1\left(1 + \frac{2f_v\beta_c}{1 - f_v\beta_c}\right) \quad (8)$$

where β_c is the depolarizing field factor of the 2D cluster,

$$\beta_c = \frac{\varepsilon(R) - \varepsilon_1}{\varepsilon(R) + \varepsilon_1}. \quad (9)$$

Note that the factor 2 (instead of 3) appears in Eq. (8) since the clusters are now cylindrical in shape for the 2D case. With these two models (A and B), we can now study the effect on molecular decay rates due to the distribution of roughness at the interface.

NUMERICAL RESULTS AND DISCUSSION

We have performed some computation using both Eqs. (7)-(9) and (3) together with (1) for the system studied previously using only the MG model.[15] Thus we have the mole-

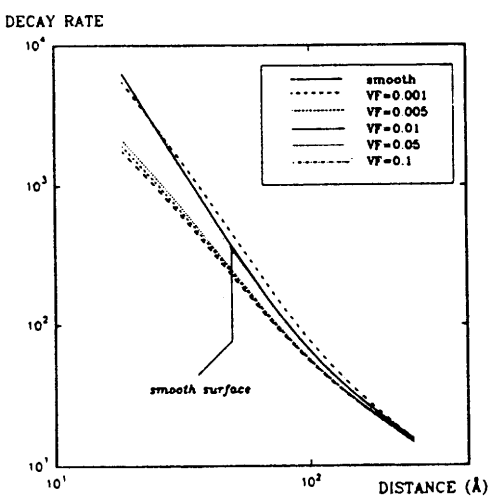

Fig. 2. Same as Fig. 1, except that the island size is fixed at a = 5 Å while the volume fraction is varied from 0.1% to 10%. Only the results from the FC model are shown in the graph.

cule emitting at a wavelength of 3800 Å in a medium with ε_1 = 1.7, and the substrate is taken to be silver throughout, with the optical constants for silver available from the literature.[23] Fig. 1 shows the results for the normalized decay rates versus molecule-surface distances (d) for different values of the surface island radius for both the MG and the FC models. It is clear that the case where the islands are clustered leads to a diminution of the induced-decay rates as compared to the case where they are disperse throughout the interface layer. Futhermore, while almost all the results obtained in this calculation within the range of the set of the parameters give results smaller than those for the flat-surface case, "crossing" does occur between the flat surface and the MG curves. It can also occur with the FC curves for another set of parameters (see below). Thus it confirms once again that the presence of surface roughness can lead to *both* the possibilities of enhancing or suppressing the induced-decay rates for the admolecules as observed in various modeling studies.[7,12]

It is also remarkable to see the significant effects due to surface roughness at such close distances even for the slight presence of roughness at the interface (only 1% in volume fraction in this case). Fig. 2 shows similar decay-rate plots (versus d) for the FC model for different values of the volume fraction of the islands. While suppression from the flat surface values is seen once again, one can see that as the "amount of metal" increases in the interfacial layer, dissipation leads to larger nonradiative decay and hence less suppression. Crossing between the FC and the flat curves finally take place for V_F roughly above 5%. We also performed a similar calculation with the MG model and found that just like the case in Fig. 1, most results are greater than those from the FC modeling, and crossing with the flat surface curve occurs at a very low value of volume fraction at

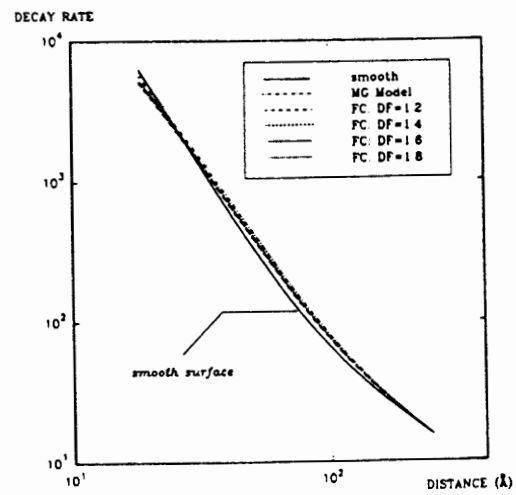

Fig. 3. Same as Fig. 1, except that both the volume fraction and the island size are fixed at 0.01 and 5 Å, respectively. The fractal dimension (DF ≡ d_f) is varied from 1.2 to 1.8 in the FC model.

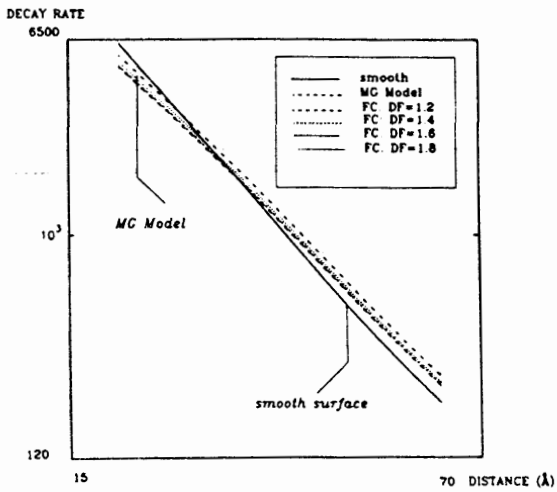

Fig. 4. An enlarged portion of Fig. 3.

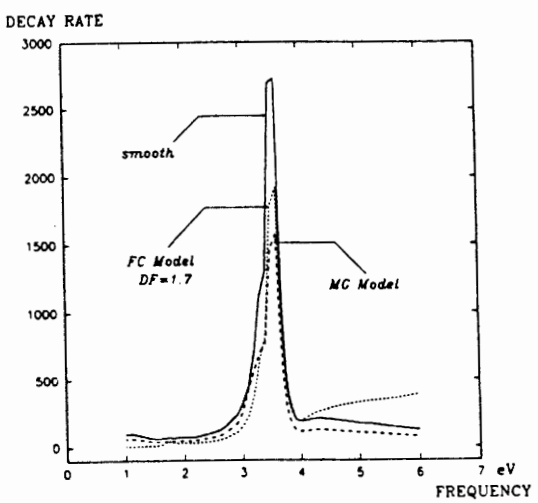

Fig. 5. Normalized induced-decay rate versus emission frequency of the admolecule for the flat- surface case, the MG model, and the FC model, respectively. The molecule-surface distance is fixed at 50 Å, and all other parameters are as in Fig. 3.

roughly something above 0.5%. Figs. 3 and 4 show again similar plots with the FC factal dimension varied. This shows qualitatively the effect due to different "degree of clustering" among the islands. We see that while the overall results are not very sensitive to this factor, surface-induced damping does increase with the fractal dimension, and beyond a certain critical value of d_f (~ 1.8), the FC results become greater than those from the MG modeling. We should also mention that aside from being insensitive to the parameter d_f in the FC model, the results are also completely insensitive to the cluster size. We have varied R/a from 5 to 50 and seen no appreciable change in the results. Fig. 5 shows a plot of induced-decay rates versus emission frequency of the molecule for a distance fixed at d = 50 Å. We see that while the different cases (flat, MG, FC) give slightly different values for the decay rates, the resonant positions are almost identical and are all at roughly the flat-surface plasmon resonance frequency for silver (~ 3.5 eV). This is consistent with previous results obtained by modeling the island surface as a periodic 2D array of spheres in which it was found that the nonradiative decay rates are quite insensitive to the geometrical structure of the substrate islands.[13] This is so for our calculation since at such a close distance of 50 Å, we expect that the total decay rate is mainly nonradiative in nature.

CONCLUSION

Within the mean field theory approach, we have studied the effect of surface roughness on the decay rates for admolecules in the vicinity of an island surface, paying particular attention to the role of the distribution of roughess at the interface. We believe that our modeling results can be tested since as mentioned above, fractal-clustering behavior among the islands was indeed observed in metal-on-metal growth processes. In comparison with previous modeling work which treats the surface islands as individual particles without averaging them over the interfacial layer,[13] our approach is highly simplified but limited in the sense that we cannot model the situation where the admolecule falls within the so-called "cavity site" at the interface. Morever, our approach allows us to study different configurations for the distribution of the surface islands which would be otherwise extremely difficult without resorting to an all-numeric approach via computer simulation. Furthermore, as we have seen, the results obtained within this simple approach are quite consistent with previous results such as the possibility of both enhancing and suppressing flat-surface-induced decay rates due to the presence of roughness,[7,12] as well as the insensitivity of the decay rates to the details of the island configurations at close molecule-surface distances.[13]

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Key Words

Admolecule; Fractal cluster; Decay rate; Island surface.

REFERENCES

1. Ford, G.W.; Weber, W. H. *Phys. Reports* **1984**, *113*, 195; Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783; Leung, P.T.; George, T. F. *Spectroscopy* **1989**, *4*, 35.
2. Chance, R. R.; Prock, A.; Silbey, R. *Adv. Chem. Phys.* **1978**, *37*, 1.
3. Rossetti, R.; Brus, L. E. *J. Chem. Phys.* **1982**, *76*, 1146.
4. Alivisatos, A. P.; Waldeck, D. H.; Harris, C. B. *J. Chem. Phys.* **1985**, *82*, 541.
5. Persson, B. N. J.; Lang, N. D. *Phys. Rev. B* **1982**, *26*, 5409.
6. Arias, J.; Aravind, P. K.; Metiu, H. *Chem. Phys. Lett.* **1982**, *85*, 404.
7. Leung, P. T.; George, T. F. *Phys. Rev. B* **1987**, *36*, 4664.
8. Weber, W. H.; Ford, G. W. *Phys. Rev. Lett.* **1980**, *44*, 1774.
9. Leung, P. T. *Phys. Rev. B* **1990**, *42*, 7622; Leung, P. T.; Hider, M. H. *J. Chem. Phys.* **1993**, *98*, 5019.
10. Ahmadi, M. F.; Rusling, J. F. *Langmuir* **1991**, *7*, 1529.
11. Ruppin, R. *J. Chem. Phys.* **1982**, *76*, 1681.
12. Kim, Y. S.; Leung, P. T.; George, T. F. *Surf. Sci.* **1988**, *195*, 1.
13. Liver, N.; Nitzan, A.; Freed, K. F. *J. Chem. Phys.* **1985**, *82*, 3831.
14. Maxwell-Garnett, J. C. *Philos. Trans. R. Soc. London Ser. A* **1904**, *203*, 385; **1906**, *205*, 237.
15. Li, X. S.; Lin, D. L.; George, T. F. *Phys. Rev. B* **1990**, *41*, 8107.
16. Li, X. S.; Lin, D. L.; George, T. F.; Liu, Y.; Gou, Q. *Phys. Lett. A* **1990**, *145*, 444.
17. Kovacs, G. J.; Scott, G. D. *Phys. Rev. B* **1977**, *16*, 1297.

18. Pines, D.; Huppert, D.; Avnir, D. *J. Chem. Phys.* **1988**, *89*, 1177.
19. See, e.g., Zhang, Z.; Chen, X.; Lagally, M. G. *Phys. Rev. Lett.* **1994**, *73*, 1829 and references therein.
20. Hui, P. M.; Stroud, D. *Phys. Rev. B* **1986**, *33*, 2163.
21. Chang, C. Y.; Kuo, L. C.; Hui, P. M. *Phys. Rev. B* **1992**, *46*, 14505.
22. Leung, P. T.; Pollard-Knight, D.; Malan, G. P.; Finlan, M. F. *Sensors and Actuators*: B **1994**, *22*, 175.
23. Palik, E. D. Ed., " *Handbook of Optical Constants of Solids*" (Academic, New York, **1985**), p 350.